Carbonaceous Species Methods Comparison Study: Interlaboratory Round Robin Interpretation of Results

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ACKNOWLEDGEMENTS

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SUMMARY AND CONCLUSIONS

Examination of the Carbonaceous Species Methods Comparison Study (CSMCS) round robin data shows that most laboratories, using a variety of thermal analytical systems, can accurately measure aerosol particulate total carbon (TC) within 5% of the group value. For TC, the group average is probably close to the true value established by laboratory-produced standards. However, organic carbon (OC) and elemental carbon (EC) measurements for similar ambient aerosol samples showed 6-9% and 28-31% variations from common averages, respectively. These variations are due to differences in the analytical systems and analysis protocols among laboratories. System differences involve the methods used to correct for pyrolysis of OC to EC during OC analysis, the maximum temperatures used in OC and EC analysis, and possibly the temperature steps and oxidation environments used in analysis protocols. Laboratories correct for pyrolysis by: 1) using a laser optical system to monitor sample laser light reflectance or transmission during the analysis; 2) minimizing pyrolysis by particular features of their system, such as the use of manganese dioxide as an oxidant; 3) making no corrections for pyrolysis and defining the OC and EC measured as "apparent OC" and "apparent EC".

Three laboratories--Desert Research Institute (DRI), Oregon Graduate Institute (OGI), and Sunset--employ optical systems to correct for pyrolysis. One would expect these laboratories to obtain similar OC and EC values. However, the CSMCS results showed that DRI and OGI, which used reflectance pyrolysis correction, obtained OC values that were similar but near the low end of the OC range. Sunset, which used transmission pyrolysis correction, obtained OC values near the high end of the OC range. EMSI and the Environmental Protection Agency (EPA), which use similar thermal systems, obtained similar OC values which were usually the highest OC values measured. Since these laboratories do not correct for pyrolysis, their OC results should fall near the lower end of the spectrum. These anomalies may result from analysis temperature differences but this cannot be established using CSMCS data. For EC, the laboratory rank order is essentially reversed. DRI\OGI obtained EC

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values near the high end of the range and Sunset obtained EC values near the low end of the range. Because the pyrolysis correction transfers carbon initially measured as EC to OC, one would expect that carbon analysis systems which correct for pyrolysis would obtain higher OC and lower EC values than systems that do not correct for pyrolysis. Thus, DRI and OGI results are not in the expected position relative to non-optical system results, while Sunset results are in the expected position. Sunset uses the highest OC upper limit temperature among these three laboratories which may be the reason for higher OC values. For most systems the temperature profile used to heat the sample may play some role in the OC/EC split determination. It may be necessary to establish temperature landmarks in the analytical protocol to insure analytical compatibility.

Since CSMCS did not include measurement samples with known OC and EC depositions per unit of filter area, statements about OC or EC accuracy cannot be made. Using the available data, no conclusive statement can be made regarding which system produces correct or preferable OC and EC results.

The following points must be considered to establish consistent OC and EC limiting temperatures in analysis protocols:

1. All laboratories should adopt a standardized maximum OC volatilization temperature. A temperature between 550 and 650°C would seem reasonable.

2. The lowest temperature at which EC will oxidize needs to be established. This temperature should not be exceeded when OC is volatilized in an oxidizing atmosphere. When oxygen is present, EC may oxidize at temperatures as low as 400°C.

3. It is assumed that EC will not volatilize at any temperature encountered in the analysis process. It is only gasified by oxidation. A standardized highest EC oxidation temperature should be adopted by all laboratories. A temperature between 800 and 900°C would seem reasonable.

A first step in establishing system validity might be the use of sucrose OC standards to establish that a system can measure a substance which pyrolizes strongly as 100% OC. EC standards should also be measured as 100% EC. Ambient aerosol OC and EC standards should be developed and supplied to all laboratories to monitor the OC/EC split point determination.

A research program which relies heavily on specially prepared standards is required to determine which system or systems produce the most accurate OC and EC data. Features of this program are:

1.   The establishment of standardized maximum temperatures to define OC and EC.

2.   The development of standards for OC, EC and combinations of OC and EC so that all laboratories can be calibrated against common standards.

3.   All laboratories need to determine the conditions under which they produce accurate OC and EC data.

4.   The determination of the utility of transmission and reflectance thermo-optical systems to correct for pyrolysis.

If acceptable standards cannot be produced, then the conditions under which all laboratories will produce consistent OC and EC data need to be determined.

RECOMMENDATIONS

The main reason for disagreement in the measurement of organic carbon (OC) and elemental carbon (EC) among laboratories is that there is no universally accepted standard or definition for either OC or EC. Pure OC and EC along with ambient aerosol standards that reflect diversity of sources must be developed and made available to all laboratories. These standards and protocols should be developed by a well planned research effort coordinated with cooperation of all laboratories. The following specific recommendations are suggested:

1. Development and distribution of acceptable OC, EC, and combination standards to all laboratories measuring these species. EC standards and samples, produced by pyrolizing sucrose and wood smoke samples, which have been heated in a helium atmosphere to remove OC, should be developed to ensure that low temperature or inappropriate EC oxidation is not occurring in a system.

2. Development of a supply source for acceptable standards.

3. Development of protocols that require all laboratories to tune their systems to reproduce acceptable standards.

4. Resolution of OC and EC differences between laboratories using similar methods (e.g., thermo-optical reflectance and transmission systems).

5. Establishment of inter-laboratory and inter-method comparison studies, such as CSMCS, every five years or after major methodological changes to monitor and document interlaboratory consistency.

6. All laboratories should measure, within a few percent, a filter deposited sucrose standard as 100% OC and a heat treated (heated to the highest temperature used in OC analysis) EC standard as 100% EC.

I. INTRODUCTION

This section describes the reasons for measuring the TC, OC and EC components of ambient and source particulate material. It discusses the long-standing problem of various analytical systems often not producing consistent OC and EC results and briefly describes the sampling artifact of organic vapor adsorption.

A.   Background

Particulate total carbon (TC), organic carbon (OC), and elemental carbon (EC) data (TC = OC + EC) are useful in understanding particulate air pollution (Daisey, 1980; Mueller et al., 1982; Shah, 1981; Shah et al., 1986). These carbon species are often major components of both source and ambient particulate material. They are almost always significant components of combustion emissions. Fine particulate EC is a unique product of combustion. OC is a major component of secondary aerosols. Inorganic carbon (carbonates) is generally a very small fraction (less than 1-2%, Shah, 1981) of TC and is not discussed in detail in this report.

Since the late 1970's laboratories using a variety of different analytical methods have been determining particulate OC, EC and TC data (Appel et al., 1983, 1987; Cadle et al., 1983, 1990; Countess, 1990; Fung, 1990; Groblicki, 1983; Hering, 1988; Huntzicker et al., 1982; Johnson et al., 1980; Stevens et al., 1982). TC data from different laboratories are usually consistent. This occurs because accurate TC standards are available. In contrast, OC and EC measurements for the same samples determined by various laboratories have differed significantly. These differences occur because these laboratories use different analytical methods and because OC, EC and OC and EC combination standards have not been developed.

The efficient management of air quality requires valid data about the nature of air pollution (Watson et al., 1983). The California Air Resources Board (ARB) has recognized that analysis-dependent OC and EC uncertainty is detrimental to the management of particulate air pollution. In 1986, ARB and others sponsored the Carbonaceous Species Methods Comparison Study (CSMCS) laboratory intercompar-

ison study in preparation for an intensive aerosol characterization study scheduled for the California South Coast Air Basin in 1987. CSMCS was designed to aid in the resolution of carbon measurement differences among laboratories. In the analytical comparison phase of CSMCS, similar sets of 20 carbonaceous particulate material samples were prepared and distributed to 12 laboratories for analysis. Appendix A lists the laboratories which participated in the CSMCS. The sample set included four ambient particulate material samples which were each supplied in three replicate samples (12 ambient samples). There were also seven source samples including: catalyst and non-catalyst automotive emissions, diesel emissions, soot, organic aerosol created in a smog chamber, two ambient samples heavily loaded with residential wood burning emissions, and a blank filter.

B. Purpose of This Report

The objectives of this report are: 1) analysis and interpretation of the CSMCS data; and, 2) recommendation of a program to develop consistent carbon analysis. Most laboratories which measure carbon produce accurate TC values, but often produce significantly different OC and EC data when analyzing similar samples. The nature of these differences and their resolution, to produce consistent OC\EC data, are the subjects of this report.

For this project, the following tasks were performed, using the CSMCS data:

Task 1. Method Description
Task 2. Precision Calculations
Task 3. CSMCS Data Analysis
Task 4. Data Interpretation
Task 5. Reporting

C. Particulate Carbon Data

1. The Nature of Carbonaceous Particulate Material

Particulate carbon consists of a large collection of hydrocarbon compounds and relatively pure black carbon. These carbon species are usually produced in

combustion, in secondary atmospheric processes, or in biogenic processes. The sum of all particulate carbon, TC, is the easiest measure of particulate carbonaceous content to determine. Particulate TC is readily and accurately measured by many laboratories. This is possible because accurate TC standards are available.

The usefulness of TC data can be greatly enhanced by dividing TC into organic (OC) and elemental carbon (EC) components. This division has a chemical basis, but it is also dependent on the analytical processes used to measure OC and EC. Most sources of carbonaceous aerosols have distinct OC/EC ratios that can be used for source identification.

Chemically, particulate OC is composed of a large variety of hydrocarbon compounds. OC species are usually colorless or white, but can sometimes be colored. Particles from smoldering wood combustion that contain a large amount of OC may be tan or shades of orange (Rau, 1986). There is no clear dividing line between OC and EC based on compound color. As one moves to larger and larger molecules, e. g., very large aromatic molecules, OC species containing little hydrogen or oxygen, become increasingly dark or black as they make the transition to EC. To measure OC and EC the analytical system used must use a definable separation point between OC and EC. A maximum OC volatilization temperature to be used in all analytical systems needs to be specified.

EC is often referred to as graphitic carbon, free carbon, black carbon, non-volatile carbon, and soot. The term soot may be confusing because the material found in flue pipes, which is called soot, also contains OC. EC is best described as black, practically pure carbon. EC is almost exclusively generated in combustion processes. Being black, EC plays a major role in the light-absorbing properties of aerosol particles (Bergstrom, et al., 1982; Malm and Gebhart, 1988; Shah, 1981). It may have either an amorphous structure or a crystalline graphitic structure. It will not volatilize in an inert atmosphere at the temperatures used in OC and EC analysis. EC can only be gasified by oxidation. When its structure is amorphous it may oxidize at temperatures as low as 400°C, but when its structure is crystalline it may resist oxidation at temperatures as high as 700°C.

2.   Importance of Particulate Carbon Data

Accurate total carbon (TC) data are important because carbon often comprises a large mass fraction of both source emissions and ambient aerosols. In contrast, the total trace element loading of many source and ambient aerosols may not exceed a few percent of the total mass. TC data are also important in the characterization of particulate material and in source apportionment of ambient aerosols.

Approximately 10-30% of the particulate mass in typical urban airsheds is TC which is composed of 50-70% OC and 30-50% EC (Howes, 1987; Johnson and Huntzicker, 1979; Pratsinis et al., 1984; Shah, 1981; Turpin, 1989). Usually less than 2% of TC is in the carbonate form. Annual average TC concentrations considering 46 urban sites (samples collected in 1975 and stored at room temperature until analysis in 1980) range from 3.6 μg/m^3 for Helena, MT to 19.8 μg/m^3 for Burbank, CA. The average TC value was 10.3 μg/m^3 (Shah, 1981; Shah et al.,1986). In Medford, OR, an area heavily impacted by residential wood burning and carbonaceous industrial emissions, ambient TC values higher than 100 μg/m^3 have been measured (DeCesar and Cooper, 1982) and TC represented more than 40% of the total particulate mass.

OC and EC are found in both the coarse and fine particulate size fractions and are usually a large component of fine particulate material. Coarse particulate material may contain OC from biogenic sources such as pollens and plant dust or from coagulated fine mode OC. Resuspended soil and paved road dust may contain both OC and EC from motor vehicle emissions. Many OC compounds found in ambient aerosols are mutagenic or carcinogenic. EC is usually a minor component of coarse particulate material. Since almost all ambient particulate EC is a product of combustion, it originally enters the atmosphere as fine (< 2.5 μm) particulate material. Coarse EC is formed by from agglomerated material from vehicle exhaust pipes and may be a component of resuspended road dust. Rarely, it might be wind-blown coal dust or material from industrial processes such as graphite or coke production, etc.

Combustion-generated particles, which enter the atmosphere as fine particulate material, often contain large OC and EC components. Unleaded auto emissions may

be 49% OC and 39% EC, while leaded automobile emissions may be 50% OC and 5% EC (Mulbaier and Williams, 1882; Watson, 1979). Heavy duty diesel may be over 30% OC and over 50% EC. Wood smoke from low temperature smoldering combustion may contain 60% OC and less than 5% EC, while for hot flaming combustion, OC mass may shift to 5% and EC to 20% (Rau, 1986).

Secondary particulate material, which results from the atmospheric conversion of hydrocarbon vapors to particulate material, contributes to the ambient aerosol OC fraction. Because of the complexity of atmospheric chemistry, the magnitude of this contribution to ambient aerosols is not well understood. Areas such as the South Coast Air Basin usually have a large secondary OC component because atmospheric photochemical conversion conditions are favorable and hydrocarbon vapor emissions, as indicated by emission inventories, are large.

Since OC and EC are usually large components of ambient particulate mass, they play an important role in particulate source apportionment using chemical mass balance (CMB) modeling. Without OC and EC data, it may be difficult to satisfactorily apportion such sources as residential wood smoke emissions, oil burning emissions or motor vehicle emissions. Successful use of CMB modeling depends to a large extent on consistent source and ambient OC and EC data. When ambient or source OC and EC data contain analysis method-dependent differences, the results obtained in CMB modeling using these data are expected to have diminished accuracy. These error sources are often ignored. Conversely, when both ambient and source carbon particulate material data are determined by the same analytical method, source apportionment might be accurate even though OC and EC data may contain method dependent differences. The further development of general usage CMB source composition data libraries would benefit if method dependent differences in OC and EC data were eliminated.

3. Organic Vapor Adsorption on Quartz Fiber Filters

Organic vapor adsorption (OVA) is an important sampling artifact which occurs when sampling carbonaceous aerosols on the glass or quartz fiber filter media (Fitz,

1990; McDow and Huntzicker, 1986). OVA also occurs to a lesser extent on quartz fiber filters exposed to ambient air. This artifact is not a problem in a laboratory intercomparison study such as CSMCS, but is an essential element in obtaining good ambient and source particulate carbon data. During carbon analysis, OVA cannot be distinguished from particulate OC.

OVA can be measured by sampling on a quartz fiber back up filter positioned behind a Teflon filter. The front Teflon filter removes particles from the sampling stream, but does not remove vapor carbon. Thus a quartz fiber back up filter adsorbs organic vapor in the same way as a quartz fiber front filter which is collecting particulate material. One limitation of this OVA correction method is that OC vaporized from the collected particulate material may be adsorbed by the back filter and then be subtracted from the front filter OC loading causing at most a double subtraction of OC vaporized from the collected particulate material. This effect is usually small and is minimized by using low sampling velocities. Multiple sample train experiments have been conducted by several researchers (Fitz, 1990; Eatough et al., 1989) to understand OVA.

II. ANALYTICAL METHODS

This section reviews the different analytical methods that have been used to measure TC, OC and EC and describes in detail the general nature of thermal carbonaceous particulate material analysis systems. How the various thermal and thermo-optical systems differ is also described. Appendix B gives descriptions of the carbon analysis methods used by the Citrus College inter-laboratory comparison study participants.

A. Methods for TC, OC and EC Analysis

A variety of methods have been used for determining TC, OC and EC. TC can be determined by thermal methods. OC can be determined by thermal, solvent extraction, and acid digestion methods. In solvent extraction OC is dissolved from particulate material and quantified with either gas or liquid chromatography (Grundel and Novakov, 1984; Szkarlat et al., 1984). Compared to thermal methods, solvent extraction tends to underestimate OC because it is difficult to extract the total OC loading from particulate material. Acid digestion separates OC from EC by dissolving OC with an acid. This method has not been successful because it is difficult to limit acid digesting to only the OC component of particulate material. EC, being black, may be optically quantified by measuring the light absorption capability of particulate material (Rosen et al., 1978). This method is simple and reasonably accurate. However, colored particulate material such as colored OC, metallic oxides or soil components can compromise optical EC measurement. In contrast thermal measurement defines EC by the analysis method.

The most common TC, OC and EC analysis methods used today are thermal methods. These can be subdivided into purely thermal methods and thermo-optical methods which attempt to optically correct for OC to EC conversion by pyrolysis during the analytical process. Some thermal systems accomplish OC and EC separation and minimize pyrolysis by placing filter samples in direct contact with manganese dioxide (MnO_2). Other thermal systems do not correct for pyrolysis but

classify their results as "apparent" OC and EC to indicate that these results have an instrument dependency. Thermo-optical systems attempt to correct for OC pyrolysis by using a helium-neon laser beam to observe the filter sample during the analysis process. These methods can be further subdivided into systems which monitor filter reflectance and systems which monitor filter transmission (Johnson et al., 1980; Johnson, 1981; Huntzicker et al., 1982; Sunset, 1990). Table II-1 lists the analytical parameters for the various laboratories.

B.   Thermal TC, OC, and EC Analysis

Since the mid-1970s, many laboratories have measured carbonaceous particulate samples, using thermal methods, for TC, OC and EC. Some laboratories measure only TC, but most determine OC and EC and sum these to obtain TC. Most of these laboratories have developed their own analysis methods.

In most systems an aliquot of particulate material, collected on a quartz or glass fiber filter, is heated in a helium or helium/oxygen atmosphere to vaporize OC. The sample is then heated in an oxidizing atmosphere to oxidize EC. OC is removed from the sample by evaporation when the sample is heated in an inert atmosphere. EC, which does not evaporate at the temperatures used for OC analysis, remains behind to be removed by oxidation. The vaporized OC and oxidized EC (CO_2) are then detected either as CO_2 using non-dispersive infrared or converted to methane and detected with a flame ionization detector.

OC to EC pyrolysis, during the OC determination process, complicates OC and EC analysis. Some OC species thermally degrade (char) to an amorphous form of EC rather than evaporating. This pyrolyzed OC material is then erroneously detected as EC. A large amount of effort has been expended either to minimize or to account for the OC that pyrolizes to EC during the analytical process.

There are three basic types of thermal systems: 1) systems that do not attempt to correct for pyrolysis of OC to EC; 2) systems that use an optical system to correct for pyrolysis of OC; and 3) systems that are designed to minimize pyrolysis, such as those that use manganese dioxide (MnO_2). All systems use slightly different sample

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Table II-1. List of Laboratories, Their Carbon Analysis Methods, and Analytical Parameters

LABORATORY*	CARBON METHOD	CARBON FRACTION MEASUREMENTS ANALYTICAL PARAMETERS FOR		
		TOTAL (TC)	ORGANIC (OC)	ELEMENTS (EC)
GMR	Thermal	OC + EC	350°C, Air + 950°, He	950°C, Air**
EMSI	Thermal	OC + EC	600°C, He	750°C, 2% O2
ODEQ	Thermal	850°C, He/w/MnO2	600°C, He	TC – OC
EPA	Thermal	OC + EC	600°C, He	650°C, 2% O2
UM	Thermal	600°C, 2% O2	NA	NA
GGC	Thermal	OC + EC	400°C, O2	700°C, O2
ERT	Thermal MnO2 Oxidation	OC + EC	525°C, He/w/MnO2	850°C, He/w/MnO2
OGI	Thermal Optical Reflectance	OC + EC	610°C, He	750°C, 10% O2/OCR
DRI	Thermal Optical Reflectance	OC + EC	550°C, He	650° and 800°C, 2% O2/OCR
Sunset	Thermal Optical Transmission	OC + EC	700°C, He	900°C, 2% O2/OCR
AIHL	Optical Absorption	1100°C, O2	TC – EC	Optical Absorption
LBL	Optical Absorption	NA	NA	Optical Absorption

*The analytical parameters listed were employed during the Round Robin Interlaboratory study.
** 2% O2 and 98% He.
NA = Not Applicable.
OCR = Optical Correction applied to EC values.

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heating programs. These temperature/time programs have been developed to optimize system performance. It is not clear how the sample heating program affects pyrolysis in any of these systems. It is also not clear if OC vaporization from particulate material is related to the type of particulate material being analyzed. The highest temperature used in the OC analysis determines the upper limit of the OC species that will be detected and thus the amount of OC that is detected. For most systems the upper limit of OC heating is usually in the 500-600°C range. If temperatures in this range are sufficient to remove all OC from the sample has not been determined. At these temperatures or even at higher temperatures there may still be carbonaceous materials remaining in the particulate phase that contain a few hydrogen atoms, so that they may strictly be called OC. It may be useful to standardize the upper limit OC volatilization temperature. All OC that is volatilized above this temperature would then be measured as EC.

Some researchers have explored the possibility of using the amount of OC released as a function of time and temperature as a source identification signature, i.e., using the shape of the analytical system carbon output signal for source identification. This type of information, while probably of value, has not been widely used.

For each of the analytical system types, some laboratories have developed further variations. Non-optical systems may use pure helium carrier gas or they may add air or oxygen to the carrier gas during various parts of the analysis cycle. Optical systems are of two types: those which use light reflectance to monitor pyrolysis and those which use light transmission. In most current systems, EC is removed from the particulate phase by heating the sample to 700°C to 950°C in an oxidizing atmosphere. As occurs with OC, EC oxidizes over a wide temperature range, depending on its structure. Some EC has been shown to oxidize at temperatures as low as 400°C. Other EC, such as graphite and some diesel exhaust particulate material, may be difficult to oxidize even at the higher temperatures used for EC oxidation.

The highest temperature used in a carbon analytical system is limited to about 700°C when glass fiber filters are used as the sample collection medium because

filters melt at higher temperatures. Therefore , sometimes it may not be possible to make correct EC measurements for samples collected on glass fiber filters. The use quartz fiber filters is recommended to avoid filter material melting problems during OC and EC analysis.

It appears that the many variations among OC and EC analysis systems influence the determination of the OC/EC split. It remains to be shown which systems most accurately determine the OC/EC split. At least every system used should have the ability to determine the same OC/EC split point, within 5-10% of the OC/EC standard. The following factors determine the split between OC and EC:

1. The highest temperature used in OC analysis.
2. The temperature profile used in OC analysis.
3. The gaseous environment in the sample oven during analysis.
4. The method used to account for the pyrolysis of OC to EC during OC analysis.

Any examination of OC/EC split determination needs to consider the role of oxygen availability during carbon analysis. In some systems oxygen is added to the carrier gas stream during the initial phase of OC volatilization to suppress pyrolysis. It is possible that what appears as pyrolysis suppression may be the instantaneous removal of pyrolized OC as it is formed. This is acceptable as long as no EC initially present in the sample is removed. Systems that supply oxygen with manganese dioxide may also allow pyrolysis to go undetected due to the possibility of low temperature EC oxidation. It may be that pyrolytically formed EC or other sources of amorphous carbon are especially vulnerable to low temperature oxidation.

In systems where OC is vaporized in a helium atmosphere, it is necessary to consider the effects of trace oxygen contamination. It is possible to observe the effects of 3 to 4 ppm of oxygen in the helium carrier gas by observing drift of the laser signal, which shows EC oxidation, in a reflectance thermo-optical system. Usually, it is necessary to scrub oxygen from the helium carrier gas to ensure that EC is not prematurely oxidized.

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C.   Accuracy of Thermal TC, OC, and EC Measurement Methods

TC is traditionally measured accurately (± 5-10% of standard) by most laboratories. Each laboratory can determine the accuracy of TC measurements by using easily prepared standards. If TC standards were available from a common source this would eliminate the small error caused by interlaboratory standard variations. The determination of TC is straightforward. TC is measured by heating a sample in an oxidizing atmosphere which removes carbon from the sample by a combination of vaporization and oxidation processes. The amount of carbon removed is limited by the highest oven temperature used. Oven temperatures of 900°C appear to remove all particulate OC and EC.

OC and EC determination is more complicated. To date, the accuracy of OC and EC measurements cannot be determined mainly because appropriate interlaboratory OC and EC standards have not been developed. There is no consensus on what constitutes accurate OC and EC data. Since the methods of OC and EC analysis have been under development for years, even the OC and EC data for a given laboratory may change over time due to analysis method modifications.

Standards for OC, EC, and combinations of OC and EC need to be developed. All laboratories should then calibrate to these standards. In the meantime all laboratories should at least be able to quantify a sucrose standard as nearly 100% OC and a thermally treated EC standard as nearly 100% EC. It would also be useful to standardize the upper limit temperatures that define OC and EC. How to account for or minimize the pyrolysis of OC to EC during the OC analysis needs to be determined. Also, whether and under what conditions EC is oxidized or vaporized during OC analysis needs to be determined.

III. LABORATORY INTERCOMPARISON STUDIES

This section summarizes the data analysis results for the Carbonaceous Species Methods Comparison Study (CSMCS). Data were analyzed to better understand the differences among various carbon measurement methods. Some of the other interlaboratory intercomparison studies are also briefly described and summarized in Section III-B. The list of CSMCS participant laboratories and descriptions of their methodologies are included in Appendices A and B, respectively.

A.   CSMCS Results

The 1986 CSMCS was conducted under the auspices of the California Air Resources Board (Countess, 1990; Hering, 1990; Lawson and Hering, 1990; McMurry and Zhang, 1987; Turpin et al., 1990). In this study a set of 20 samples, including 12 ambient samples (4 different samples with three replicates), 7 source samples, and a blank sample, were each analyzed by 12 laboratories. EMSI collected twelve ambient samples at the Citrus College site on August 19 and 20, 1986. Source samples #7, 11, and 18 were automotive exhaust samples collected by GMR from dynamometer tests of automobiles using unleaded, diesel, and leaded fuel, respectively. Source samples #13 and 15, called wood smoke, were heavily loaded ambient PM-10 samples collected by the Oregon DEQ in Medford, OR during February 1986. Residential wood burning emissions are a large component of Medford's ambient particulate loading. Source sample #12, called soot, was a heavily loaded ambient sample which was heated in air at 300 °C for two hours to reduce OC thus producing a sample with a very large EC component. Sample #19 was a organic aerosol sample generated by photolysis of trimethylbenzene in a California Institute of Technology outdoor smog chamber. Sample #9 was a blank filter. Most of the participating laboratories did both OC and EC analysis, although some only did EC or TC. TC and OC and EC data analyses are discussed separately in Sections III-A.1 and III-A.2, respectively.

1.   Total Carbon Data

Table III-1 shows the TC data for CSMCS for the twelve participating laboratories. Each laboratory attempted to insure its analytical TC accuracy by calibration with its own external standards. Since the sample set supplied to the laboratories did not include TC standards, CSMCS data accuracy cannot be evaluated in terms of how well laboratories reproduced standard values. There are no known "correct" carbon values for any of the CSMCS samples. However, the average TC values around which most of the data closely cluster can be assumed to be a good approximations of the true values, because all sources of error can be assumed to be random.

An examination of the data shows that the OR DEQ data and the EMSI data calibrated with adipic acid are significantly below those of all the other laboratories. These two data sets have large calibration errors. The Coulomb data also seem to have problems. Coulomb measured a very high blank value. When this high blank value is subtracted from the sample set values, sample set values similar to other laboratories were produced. This suggests that there is an instrument blank or blank contamination of about 8-10 μg/cm^2 for carbon analysis. Also, one of the sample replicates showed high variability. Therefore, the Coulomb data were excluded from all laboratory averages. The laboratory TC averages include data from 10 laboratories: AIHL, DRI, EMSI(KHP), EPA, ERT, GM, Global, OGI, Sunset, and UM. Figure III-1 shows scatter plots of TC data plotted in pairs for the 10 consistent participants. These plots describe the general behavior of TC data and show that most laboratories agree with one another.

Table III-2 shows the range, average, standard deviation, and coefficient of variation (CV) values for all the samples for the 10 laboratories. The CV for each sample is the standard deviation divided by the average for all laboratories. The CV values for the ambient samples are consistently in the 6-8% range and are generally lower than CV values for source samples. The four ambient aerosol samples are most useful to determine both analysis accuracy and precision because they were supplied in triplicate and these samples are neither very lightly loaded nor overloaded. Data

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Table III–1. ARB Carbonaceous Species Methods Comparison Study Interlaboratory Round Robin Results Total Carbon Loading, ug/cm2, blank corrected, 9/22/87

SAMPLE #	TYPE	AIHL	Coul.	DRI	EMSI Adipic	EMSI KHP	EPA	ERT	GM	Global	OGI	OR DEQ	Sunset	UM
01	Day 86	38.2	37.1	38.8	31.2	38.5	35.2	37.6	39.4	38.8	37.8	24.0	38.9	42.8
10	Day 86	38.8			31.3	38.2	36.2	35.5	36.6	39.3	33.3	25.0		36.1
16	Day 86	38.4			31.4	38.7	38.0	37.7	36.9	41.7	38.4	28.0		38.3
03	Night 87	24.3	21.7	23.6	20.8	24.3	22.2	22.9	22.6	27.3	23.2	16.0	22.5	22.6
05	Night 87	24.9	17.4		21.0	24.2	22.4	23.5	24.4	25.4	24.3	18.0	23.5	21.8
14	Night 87	24.6	18.0		20.2	23.8	21.8	23.0	23.1	25.5	27.8	14.0	23.0	24.0
06	Day 96	34.9	31.5	32.8	28.7	35.3	32.0	32.1	31.9	34.8	32.0	19.0	32.2	32.7
17	Day 96	34.3		34.3	28.2	34.5	32.4	31.2	35.7	34.9	35.0	22.0		31.4
20	Day 96	34.6		34.2	27.7	35.5	32.8	33.1	32.2	35.7	33.9	24.0		29.8
02	Night 97	28.5	30.0	27.2	24.8	29.9	26.4	26.6	26.3	30.7	23.9	19.0	28.4	27.7
04	Night 97	28.8			24.4	29.0	26.6	27.2	26.9	31.1	29.0	16.0		28.0
08	Night 97	28.8			24.6	29.6	26.6	27.5	27.1	29.8	26.3	15.0		25.9
07	Cat. Buick	39.3	25.9	33.2	34.2	34.4	28.6	31.6	45.6	33.6	32.3	25.0	30.0	32.0
11	Diesel Olds	128.0	105.7	106.6	94.4	98.0	104.8	101.3	103.5	99.1	119.9	40.0	101.1	104.9
18	Pb Chevy	70.2	72.2	67.8	60.9	68.3	65.7	64.5	63.8	74.5	68.3	36.0	63.6	61.5
12	Soot	12.6	12.7	14.0	11.2	14.3	10.0	13.5	10.7	13.5	15.0	5.0	13.7	12.8
19	Org. Aeros.	10.2	1.9	9.2	9.1	9.8	8.7	9.6	9.1	8.9	6.7	1.0	7.9	7.7
13	Wood Smoke	100.0	96.3	98.3	98.7	98.7	89.1	89.9	104.5	99.5	98.4	63.0	91.2	92.2
15	Wood Smoke	387.0	407.3	328.2	409.8	383.0	335.2	366.2	469.5	404.1	393.9	228.0	332.3	373.0
09	Blank	1.3	10.7	1.6	0.0	0.0	1.4	1.0	2.5	0.6	3.4	3.0	0.6	3.7
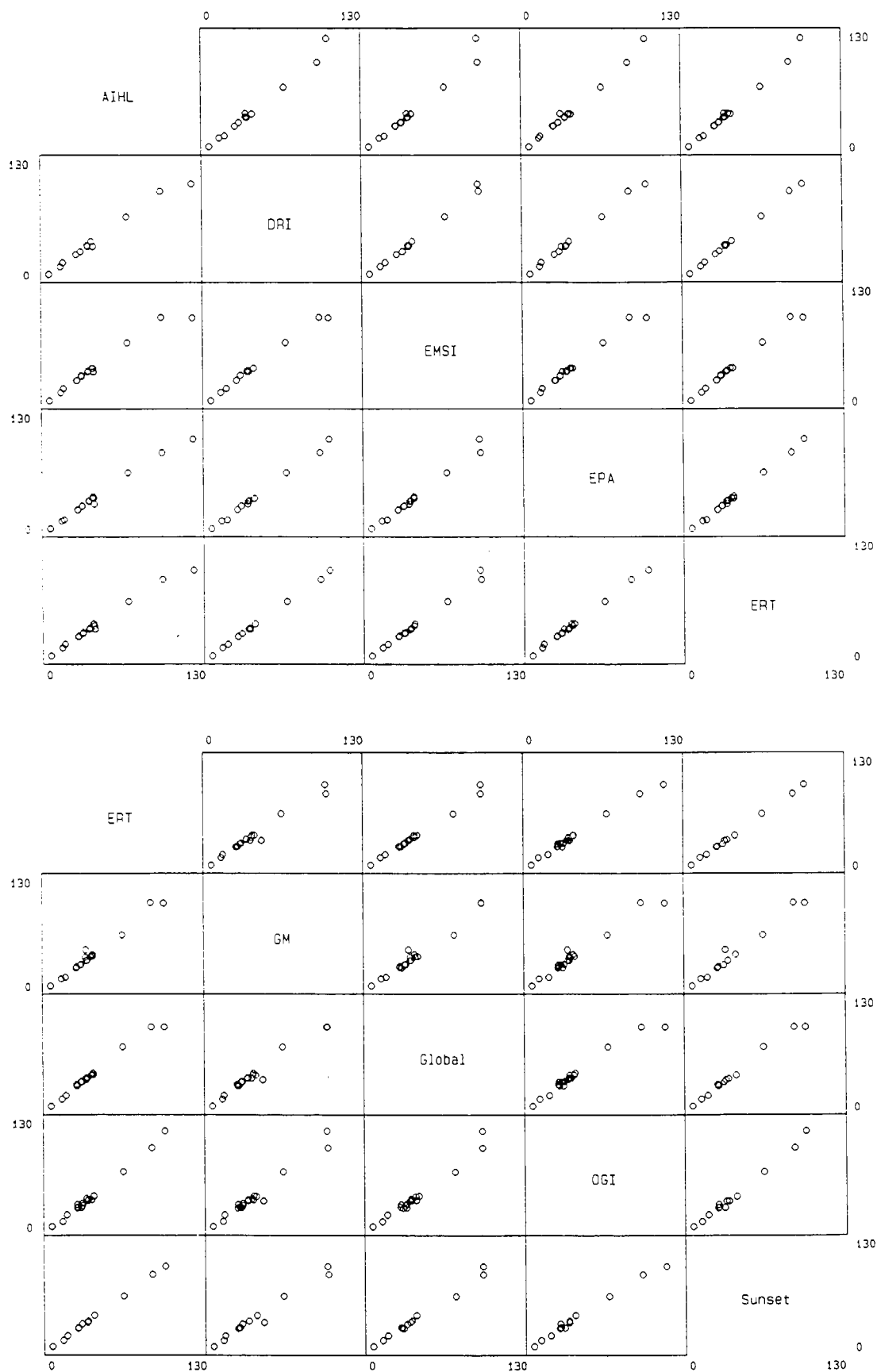
Figure III-1. Scatterplot Matrix for Total Carbon (μg/cm^2) Data for Selected Laboratories

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Table III-2. TC Data Range and Statistics (ug/cm2)

SAMPLE	TYPE	Max.	Min.	Avg.	Std.	CV%
01	Day 86	42.8	35.2	38.6	1.8	4.6
10	Day 86	39.3	33.3	36.8	1.8	5.0
16	Day 86	41.7	36.9	38.5	1.3	3.4
	Avg.	41.3	35.1	38.0	1.4	4.3
03	Night 87	27.3	22.2	23.6	1.4	6.1
05	Night 87	24.9	21.8	23.8	1.1	4.6
14	Night 87	27.8	20.2	24.1	2.0	8.1
	Avg.	26.7	21.4	23.8	1.5	6.3
06	Day 96	35.3	31.9	33.1	1.3	3.9
17	Day 96	35.7	31.2	33.7	1.6	4.6
20	Day 96	35.7	29.8	33.5	1.7	5.1
	Avg.	35.6	31.0	33.4	1.5	4.6
02	Night 97	30.7	23.9	27.6	1.9	6.7
04	Night 97	31.1	24.4	29.3	1.4	4.7
08	Night 97	29.8	24.6	29.3	1.4	4.8
	Avg.	30.5	24.3	28.7	1.5	5.4
07	Cat. Buick	45.6	28.6	34.1	4.7	13.8
11	Diesel Olds	128.0	98.0	106.7	9.2	8.6
18	Pb Chevy	74.5	61.5	66.8	3.6	5.4
12	Soot	15.0	10.0	13.0	1.5	11.4
19	Org. Aerosol	10.2	6.7	8.8	1.0	11.6
13	Wood Smoke 1	104.5	89.1	96.2	4.9	5.1
15	Wood Smoke 1	469.5	328.2	377.2	40.0	10.6
09	Blank	3.7	0.0	1.6	1.2	72.2

The sample data have been blank corrected.
CV% = Coefficient of Variation = (Avg/Std.)*100
Excludes: Coulomb, EMSI-adipic and OR DEQ.
Includes: AIHL, DRI, EMSI, EPA, ERT, GM, Global, OGI, UM, Sunset.

precision is defined by the standard deviation of the triplicate sample. The ambient data are a good measure of best carbon analytical system performance. The analysis of ambient data will catalog the performance that can be expected and the analysis of source data will show how analytical results can degrade when samples become difficult to analyze.

The diesel Olds, #13 wood smoke, and leaded Chevy samples also yielded CV values similar to the ambient data showing that they were easy to analyze and were homogeneously deposited. The catalytic Buick, soot, #15 wood smoke, and organic aerosol had CV values in the 11-13% range. The organic aerosol and soot samples may have been difficult to precisely analyze because they were lightly loaded. Wood smoke sample #15 gave more variable results because it overloaded some analysis systems.

Table III-3 shows TC for all data ratioed against the average of the ten "consistent" laboratories. The degree to which these values differ from 1.0 shows a laboratories failure to conform to the group average. For TC we assume that the group average is the best approximation of the correct value. The data inconsistencies (ratio values very different from 1.0) for Coulomb, EMSI-Adipic, and the OR DEQ are clearly shown. If the sample sets presented to all the laboratories were identical and each laboratory was able to recover all the carbon on the sample then the ratio values in Table III-3 for each laboratory would be similar for all samples. Laboratories whose TC calibration yielded higher than the group average sample TC values would have ratio values that would cluster about a consistent value greater than 1.0 and vice versa. Table III-3 shows that the ambient data ratio values for all laboratories are more consistent than the source data ratio values. For all laboratories except Global the ambient average ratio values do not differ from 1.0 by more than a few percent. For all laboratories except OGI, precision was within a few percent. The OGI data had a few replicate values which were very different from what appeared to be the correct value. Since these differences were both high and low, the reasons for the differences are not apparent. Both DRI and Sunset ran replicates on one ambient

Table III-3. Ratio of the TC Value for the Indicated Laboratories to the Average of Ten Consistent Laboratories

SAMPLE	TYPE	AIHL	Coul.	DRI	EMSI Adipic	EMSI KHP	EPA	ERT	GM	Global	OGI	OR DEQ	Sunset	UM
01	Day 86	0.99	0.96	1.01	0.81	1.00	0.91	0.97	1.02	1.01	0.98	0.62	1.01	1.13
10	Day 86	1.06			0.85	1.04	0.99	0.97	1.00	1.07	0.91	0.68		1.00
16	Day 86	1.00			0.82	1.00	0.99	0.98	0.96	1.08	1.00	0.73		1.02
03	Night 87	1.03	0.92	1.00	0.88	1.03	0.94	0.97	0.96	1.16	0.99	0.68	0.96	0.97
05	Night 87	1.05	0.73		0.88	1.02	0.94	0.99	1.02	1.07	1.02	0.76	0.99	0.93
14	Night 87	1.02	0.75		0.84	0.99	0.91	0.96	0.96	1.06	1.16	0.58	0.96	1.01
06	Day 96	1.06	0.95	0.99	0.87	1.07	0.97	0.97	0.96	1.05	0.97	0.57	0.97	1.00
17	Day 96	1.02		1.02	0.84	1.02	0.96	0.92	1.06	1.03	1.04	0.65		0.95
20	Day 96	1.03		1.02	0.83	1.06	0.98	0.99	0.96	1.06	1.01	0.72		0.90
02	Night 97	1.03	1.09	0.99	0.90	1.08	0.96	0.97	0.95	1.11	0.87	0.69	1.03	1.01
04	Night 97	0.98			0.83	0.99	0.91	0.93	0.92	1.06	0.99	0.55		0.97
08	Night 97	0.98			0.84	1.01	0.91	0.94	0.93	1.02	0.90	0.51		0.90
Ambient Avg.		1.02	0.90	1.00	0.85	1.03	0.95	0.96	0.97	1.07	0.98	0.64	0.98	0.98
Std.		0.03	0.13	0.01	0.03	0.03	0.03	0.02	0.04	0.04	0.07	0.07	0.03	0.06
CV%		2.50	13.93	1.19	3.25	2.93	3.16	2.12	4.09	3.68	7.27	11.44	2.77	6.05
07	Cat. Buick	1.15	0.76	0.97	1.00	1.01	0.84	0.93	1.34	0.99	0.95	0.73	0.88	0.94
11	Diesel Olds	1.20	0.99	1.00	0.88	0.92	0.98	0.95	0.97	0.93	1.12	0.37	0.95	0.99
18	Pb Chevy	1.05	1.08	1.01	0.91	1.02	0.98	0.97	0.95	1.11	1.02	0.54	0.95	0.93
12	Soot	0.97	0.98	1.08	0.86	1.10	0.77	1.04	0.82	1.04	1.15	0.38	1.05	1.00
19	Org. Aeros.	1.16	0.22	1.05	1.04	1.12	0.99	1.09	1.04	1.01	0.76	0.11	0.90	0.87
13	Wood Smoke	1.04	1.00	1.02	1.03	1.03	0.93	0.93	1.09	1.03	1.02	0.66	0.95	0.96
15	Wood Smoke	1.03	1.08	0.87	1.09	1.02	0.89	0.97	1.24	1.07	1.04	0.60	0.88	0.98
Source Avg.		1.09	0.87	1.00	0.97	1.03	0.91	0.98	1.06	1.03	1.01	0.49	0.94	0.95
Std.		0.08	0.29	0.06	0.08	0.06	0.08	0.06	0.16	0.06	0.12	0.20	0.06	0.04
CV%		7.30	32.73	6.13	8.23	5.85	8.57	5.73	15.41	5.38	11.80	40.23	5.93	4.23
09	Blank	0.89	7.31	1.09	0.00	0.00	0.96	0.68	1.71	0.41	2.32	2.05	0.41	2.53

Lab group average excludes: Coulomb, EMSI–adipic and OR DEQ.
Lab group average includes: AIHL, DRI, EMSI, EPA, ERT, GM, Global, OGI, UM, Sunset.

sample, so precision data are very limited for these laboratories. Usually, the ten laboratories were all able to recover a similar amount of carbon from these samples.

For the source samples, most laboratories showed some ratio values that differed from 1.0 by more than 10%. Only the #13 wood smoke sample appeared homogeneous across all the laboratories. One would expect the ratio values for sources to be similar to the ambient average ratio values if all the samples were homogeneous and carbon recovery was complete for all laboratories. It appears that the catalyst equipped Buick, the diesel Olds, soot, and organic aerosol and #15 wood smoke source samples showed large differences at least for some of the laboratories. The wood #15 smoke sample was too heavily loaded for some of the analytical systems. Some combination of sample non-homogeneity and variations among laboratories in recovering refractory EC can probably explain the differences for these filter samples. The combination of these effects can differ from sample to sample. If the differences were primarily due to differences in carbon recovery one would expect laboratories heating samples to the highest temperatures to have the largest recovery. The differences not explained by sample recovery must be due to sample inhomogeneity and random errors.

The average values for the each laboratory's ambient data can be used to assess how each laboratory's TC calibration compared to the laboratory average, i. e., how closely it compared to the best estimate of the true TC value. It is assumed that the average of all TC data is the best estimate of true TC values. Therefore the major comparison of TC results across laboratories will be focused on ambient data.

Table III-3 shows that most laboratories occasionally measured values for a given sample, especially for source samples, which were significantly different from the values measured by most other laboratories. These different results influence the group average and thus the ratio values obtained by all other laboratories. It would be desirable to have a "dependable" standard of comparison. Choosing one laboratory as the standard of comparison, at the least, eliminates variations in sample recovery from the comparison. Table III-4 shows TC data ratioed against AIHL data. AIHL data were chosen as a comparison standard because AIHL obtained consistent replicate

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Table III-4. TC Values of Indicated Laboratory Ratioed to to AIHL Values

SAMPLE	TYPE	DRI	EMSI	EPA	ERT	GM	Global	OGI	Sunset	UM
01	Day 86	1.02	1.01.	0.92	0.98	1.03	1.02	0.99	1.02	1.12
10	Day 86		0.98	0.93	0.91	0.94	1.01	0.86		0.93
16	Day 86		1.01	0.99	0.98	0.96	1.09	1.00		1.00
03	Night 87	0.97	1.00	0.91	0.94	0.93	1.12	0.95	0.93	0.93
05	Night 87		0.97	0.90	0.94	0.98	1.02	0.98	0.94	0.88
14	Night 87		0.97	0.89	0.93	0.94	1.04	1.54	0.93	0.98
06	Day 96	0.94	1.01	0.92	0.92	0.91	1.00	0.92	0.92	0.94
17	Day 96	1.00	1.01	0.94	0.91	1.04	1.02	1.02		0.92
20	Day 96	0.99	1.03	0.95	0.96	0.93	1.03	0.98		0.86
02	Night 97	0.95	1.05	0.93	0.93	0.92	1.08	0.80	1.00	0.97
04	Night 97		1.01	0.92	0.94	0.93	1.08	1.01		0.97
08	Night 97		1.03	0.92	0.95	0.94	1.03	0.91		0.90
Ambient	Avg.	0.98	1.01	0.93	0.94	0.96	1.04	1.00	0.96	0.95
	Std.	0.03	0.02	0.02	0.02	0.04	0.04	0.18	0.04	0.07
	CV%	2.66	2.21	2.69	2.40	4.14	3.49	17.76	3.85	6.87
07	Cat. Buick	0.84	0.88	0.73	0.80	1.16	0.85	0.82	0.76	0.81
11	Diesel Olds	0.83	0.77	0.82	0.79	0.81	0.77	0.94	0.79	0.82
18	Pb Chevy	0.97	0.97	0.94	0.92	0.91	1.06	0.97	0.91	0.88
12	Soot	1.11	1.13	0.79	1.07	0.85	1.07	1.19	1.09	1.02
19	Org. Aeros.	0.90	0.96	0.85	0.94	0.89	0.87	0.66	0.77	0.75
13	Wood Smoke	0.98	0.99	0.89	0.90	1.05	1.00	0.98	0.91	0.92
15	Wood Smoke	0.85	0.99	0.87	0.95	1.21	1.04	1.02	0.86	0.96
Source	Avg.	0.93	0.96	0.84	0.91	0.98	0.95	0.94	0.87	0.88
	Std.	0.09	0.10	0.06	0.09	0.15	0.11	0.15	0.11	0.09
	CV%	10.07	10.99	7.50	9.63	14.92	11.48	16.38	12.08	9.68
09	Blank	1.23	0.00	1.08	0.77	1.92	0.46	2.62	0.46	2.85
Overall	Avg.	0.95	0.99	0.90	0.93	0.97	1.01	0.98	0.91	0.92
	Std.	0.08	0.07	0.06	0.06	0.10	0.08	0.17	0.09	0.08
	CV%	7.92	7.14	6.69	6.27	9.86	8.38	17.53	10.10	8.69

CV% = Coefficient of Variation = (Avg./Std.)x100

values for the ambient data and used 1100°C as the highest temperature in the analysis. Using AIHL data as a comparison standard eliminates, at least for ambient data, the effect of random deviating measurements from influencing the comparison standard.

For source data, the ratio differences among laboratories are probably due to differences in sample homogeneity and carbon recovery. Since the ratios are generally less than 1.0, it would seem that most laboratories have lower recovery efficiencies than AIHL. Ratio values that are higher than the average for a given laboratory may show sample inhomogeneities.

Table III-5 shows TC averages for the three replicates of the four ambient samples. The last column in the table shows that the average CV for all laboratories was less than 5%. Precision for most labs was in the 1-3% range. OGI and UM precisions were usually in the 4-8% range.

The ratios of average values for the four ambient samples to the average of all laboratories are included in Table III-3. These values show the day-to-day consistency within labs. The average value of these ratios is the best measure of how the absolute TC calibrations of the labs are related to each other when the CSMCS data set was analyzed.

Most TC measurement uncertainty probably results from calibration uncertainty, incomplete sample recovery, filter deposit non-homogeneity and sample punch area uncertainty. Since the TC uncertainty in the CSMCS was around 5%, it may well be that this is near the lower limit that can be expected.

2.   Organic and Elemental Carbon Data

Tables III-6 and III-7 show the OC and EC data for CSMCS for the 12 participating laboratories.   Tables III-8 and III-9 show the range, average, and standard deviation, and coefficient of variation for all the samples in the CSMCS sample set. OC or EC data from Coulomb, EMSI calibrated with adipic acid and the Oregon DEQ are not included in the scatter plots and in the following analyses for the reasons discussed earlier. UM data are also not included, because they measure only

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Table III-5: Summary Statistics for Ambient TC Data (ug/cm2)

	AIHL	DRI	EMSI	EPA	ERT	GM	Global	OGI	Sunset	UM	Avg. All Labs*
Day 86											
Avg.	38.47	38.80	38.47	36.47	36.93	37.63	39.93	36.50	38.90	39.07	38.1
Std.	0.25		0.21	1.16	1.01	1.26	1.27	2.28		2.79	1.1
CV%	0.65		0.53	3.18	2.75	3.34	3.17	6.24		7.14	2.9
Night87											
Avg.	24.60	23.60	24.10	22.13	23.13	23.37	26.07	25.10	23.00	22.80	23.8
Std.	0.24		0.22	0.25	0.26	0.76	0.87	1.96	0.41	0.91	1.1
CV%	1.00		0.90	1.13	1.13	3.25	3.35	7.81	1.77	3.99	4.7
Day 96											
Avg.	34.60	33.77	35.10	32.40	32.13	33.27	35.13	33.63	32.20	31.30	33.4
Std.	0.24	0.68	0.43	0.33	0.78	1.72	0.40	1.24		1.19	1.3
CV%	0.71	2.03	1.23	1.01	2.42	5.19	1.15	3.68		3.79	3.8
Night97											
Avg.	28.70	27.20	29.50	26.53	27.10	26.77	30.53	26.40	28.40	27.20	27.8
Std.	0.14		0.37	0.09	0.37	0.34	0.54	2.08		0.93	1.3
CV%	0.49		1.27	0.36	1.38	1.27	1.78	7.89		3.41	4.7
Averages of the above data											
Avg.	31.59	30.84	31.79	29.38	29.83	30.26	32.92	30.41	30.63	30.09	30.8
Std.	0.22		0.31	0.46	0.61	1.02	0.77	1.89		1.45	1.21
CV%	0.71		0.98	1.42	1.92	3.26	2.36	6.41		4.58	4.05

CV% = Coefficient of Variation = (Avg/Std.)x100
Where no Std. and CV% values are shown the avg. values are a single measurement.
* Excludes Coulomb, EMSI-Adipic, and OR DEQ

Table III–6. ARB Carbonaceous Special Methods Comparison Study Interlaboratory Round Robin Results, Organic Carbon Loading, (ug/cm2), blank corrected   9/22/87

SAMPLE	TYPE	AIHL	Coul.	DRI	EMSI Adipic	EMSI KHP	EPA	ERT	GM (Un)	GM (Pre)	Global	OGI	OR DEQ	Sunset
01	Day 86	29.7	29.2	26.7	26.3	32.4	30.8	29.5	26.8	29.2	27.2	27.3	21	32.4
10	Day 86	30.1			26.3	31.5	32.3	27.7	25.3	27.9	27.9	22.5	15	
16	Day 86	29.8			25.8	31.3	34.1	30.7	26.2	25.4	29.6	27.3	21	
03	Night 87	18.5	19	16.5	17.5	19.9	19.6	19.2	16.5	17.1	19.3	17.9	13	19.4
05	Night 87	18.9	10.7		17.4	19.9	19.8	18.8	17.9	18.4	18.2	17.3	16	20.3
14	Night 87	18.7	11.1		17.2	19.8	19.2	18.7	16.5	17.9	18.6	20.5	11	19.7
06	Day 96	27.3	21.8	23	24.6	29.2	28.6	26	23.2	25.9	25	23.7	17	28.4
17	Day 96	26.9		24.2	23.4	28.8	29.2	25.6	25.3	28	24.5	25.9	18	
20	Day 96	26.9		23.8	23.5	29.8	29.2	26.3	23.3	25.9	24.7	24.8	17	
02	Night 97	21.9	23.9	19	21.4	24.4	24.2	22.5	18.7	21.5	22.6	16.6	18	24.1
04	Night 97	22			21.1	24	24.9	22.7	19.4	22.3	22.9	21.7	16	
08	Night 97	21.9			20.8	24	24.6	23.5	19.7	20	22.2	18.5	12	
07	Cat. Buick	22.8	0.6	5.6	10.7	11	13.9	8.5	11.8	9.6	8.3	5.6	8	9.7
11	Diesel Olds		8.2	14.3	11.8	14	29.7	15.6	18	18.8	15.4	37.8	12	12.6
18	Pb Chevy	62.2	50.7	39.8	47.5	56.1	64	54.1	37.3	44.8	46.5	45.5	36	50.1
12	Soot	7.5	1.6	1.2	2.7	5.4	5	4.3	1.7	2.5	4.1	2.9	33	2.9
19	Org. Aeros.	10.2	2.2	8.9	9.1	9.6	8.2	8.8	8.1	7.8	7.8	6.7	2	7.9
13	Wood Smoke 1	83	88	62.5	87.2	89.5	83.8	86.1	75.7	82.4	92.9	71.8	47	82.7
15	Wood Smoke 15		398	253.5	383	366.3	257.6	364.7	381.5	390.5	392.1	299.2	195	320.5
09	Blank	1.3	7.1	1.2	0	0	1.2	1	2.5	2.5	0.7	3.4	2	0.6

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Table III-7. ARB Carbonaceous Species Methods Comparison Study Interlaboratory Round Robin Results Elemental Carbon Loading, ug/cm2 blank corrected   9/28/87

SAMPLE	TYPE	AIHL	Coul.	DRI	EMSI Adipic	EMSI KHP	EPA	ERT	GM (Un)	GM (Pre)	Global	LBL	OGI	OR DEQ	Sunset
01	Day 86	8.5	8	12.2	4.9	6.1	4.4	8.2	12.5	10.2	11.4	7.9	10.4	3	6.3
10	Day 86	8.7			5	6.7	3.9	7.8	11.3	8.7	11.3	7.3	10.8	10	
16	Day 86	8.5			5.5	7.4	4	7	10.7	11.5	12	7.6	11.1	7	3
03	Night 87	5.8	2.7	7.2	3.2	4.4	2.7	3.7	6.1	5.5	7.9	5	5.3	3	3.1
05	Night 87	6	6.6		3.6	4.3	2.6	4.7	6.5	6	7.1	5	7	2	3.3
14	Night 87	5.9	6.8		3.1	4	2.6	4.3	6.6	5.2	6.8	5.2	7.3	3	3.7
06	Day 96	7.5	9.7	9.8	4.1	6.1	3.4	6.1	8.7	6	9.7	6	8.3	2	
17	Day 96	7.4		10.1	4.9	5.7	3.2	5.6	10.4	7.7	10.3	6.4	9	4	
20	Day 96	7.7		10.4	4.2	5.7	3.6	6.9	8.8	6.3	10.9	6.3	9.1	7	
02	Night 97	6.6	6	8.3	3.4	5.5	2.2	4.1	7.6	4.8	8	5.9	7.3	1	4.2
04	Night 97	6.8			3.2	5	1.7	4.5	7.5	4.6	8	5.8	7.4	0	
08	Night 97	6.9			3.8	5.6	2	4	7.3	7.1	7.5	6.2	7.8	3	
07	Cat. Buick	16.5	25.3	27.7	23.4	23.4	14.7	23	33.8	36	25.3	11.3	26.7	17	20.2
11	Diesel Olds		97.5	92.4	82.6	84	75.1	85.7	85.3	84.7	83.6	15.5	82.1	28	88.4
18	Pb Chevy	8	21.5	28.1	13.4	12.2	1.7	10.4	26.5	19	27.8	5.8	22.8	0	13.4
12	Soot	5.1	11.1	12.9	8.5	8.9	5	9.2	9	8.2	9.2	3.2	12.1	2	10.7
19	Org. Aeros	0	0	0.4	0	0.2	0.5	0.8	0.97	1.3	1	0	0	0	0
13	Wood Smo	16.5	8.3	35.8	11.6	9.2	5.3	3.8	28.5	21.8	6.5	11.2	26.6	16	8.4
15	Wood Smoke	9.3		74.8	26.8	16.7	77.6	1.6	87.4	78.7	11.9	12	94.7	33	11.7
09	Blank	0	3.6	0.3	0	0	0.2	0.02	0	0	-0.05	0	0	1	0.08

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Table III-8. OC Data Range and Statistics Values. (ug/cm2)

SAMPLE	TYPE	Max.	Min.	Avg.	Std.	CV%
01	Day 86	32.4	26.7	29.2	2.1	7.10
10	Day 86	32.3	22.5	28.2	3.0	10.70
16	Day 86	34.1	25.4	29.3	2.7	9.20
Avg. of Day 86		32.9	24.9	28.9	2.6	9.0
03	Night 87	19.9	16.5	18.4	1.2	6.7
05	Night 87	20.3	17.3	18.8	0.9	5.0
14	Night 87	20.5	16.5	18.8	1.1	5.9
Avg. of night 87		20.2	16.8	18.7	1.1	5.9
06	Day 96	29.2	23.0	26.0	2.2	8.4
17	Day 96	29.2	24.2	26.5	1.7	6.5
20	Day 96	29.8	23.3	26.1	2.1	8.2
Avg. of Day 96		29.4	23.5	26.2	2.0	7.7
02	Night 97	24.4	16.6	21.6	2.5	11.6
04	Night 97	24.9	19.4	22.5	1.5	6.8
08	Night 97	24.6	18.5	21.8	2.1	9.5
Avg. of Night 97		24.6	18.2	21.9	2.0	9.3
07	Cat. Buick	22.8	5.6	10.7	4.7	44.19
11	Diesel Olds	37.8	12.6	19.6	8.0	40.95
18	Pb Chevy	64.0	37.3	50.0	8.5	17.00
12	Soot	7.5	1.2	3.8	1.8	48.06
19	Org. Aeros.	10.2	6.7	8.4	1.0	11.34
13	Wood Smoke	92.9	62.5	81.0	8.4	10.41
15	Wood Smoke	392.1	253.5	336.2	52.1	15.51
09	Blank	3.4	0.0	1.4	1.0	68.55

CV% = Coefficient of Variation = (Avg/Std.)x100
Excludes: Coulomb, EMSI-adipic and OR DEQ.
Includes: AIHL, DRI, EMSI, EPA, ERT, GM, Global, OGI, Sunset.

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Table III-9. EC Data Range and Statistics (ug/cm2)

SAMPLE	TYPE	Max.	Min.	Avg.	Std.	CV%
01	Day 86	12.5	4.4	8.9	2.5	28.4
10	Day 86	11.3	3.9	8.5	2.3	27.0
16	Day 86	12.0	4.0	8.9	2.5	28.2
Avg. of Day 86		11.9	4.1	8.8	2.4	27.9
03	Night 87	7.9	2.7	5.1	1.6	30.2
05	Night 87	7.1	2.6	5.2	1.5	28.4
14	Night 87	7.3	2.6	5.1	1.5	29.0
Avg. of Night 87		7.4	2.6	5.2	1.5	29.2
06	Day 96	9.8	3.4	6.8	2.1	30.2
17	Day 96	10.4	3.2	7.6	2.3	30.0
20	Day 96	10.9	3.6	7.6	2.1	28.3
Avg. of Day 96		10.4	3.4	7.3	2.2	29.5
02	Night 97	8.3	2.2	5.9	1.8	31.1
04	Night 97	8.0	1.7	5.7	1.9	33.0
08	Night 97	7.8	2.0	6.0	1.8	29.9
Avg. of Night 97		8.0	2.0	5.9	1.8	31.3
07	Cat. Buick	36.0	11.3	23.5	7.3	30.9
11	Diesel Olds	92.4	15.5	77.7	21.1	27.2
18	Pb Chevy	28.1	1.7	16.0	8.9	55.9
12	Soot	12.9	3.2	8.5	2.9	33.8
19	Org. Aeros.	1.3	0.0	0.5	0.5	97.1
13	Wood Smoke	35.8	3.8	15.8	10.3	65.5
15	Wood Smoke	94.7	1.6	46.7	36.5	78.1
09	Blank	0.3	-0.1	0.1	0.1	201.6

CV% = Coefficient of Variation = (Avg/Std.)x100
Excludes: Coulomb, EMSI-adipic and OR DEQ.
Includes: AIHL, DRI, EMSI, EPA, ERT, GM, Global, OGI, Sunset.

total carbon. These tables show that OC and EC data varied more from laboratory to laboratory than TC data. For ambient samples, CV for organic carbon ranged from 8-10% and CV for elemental carbon was about 30%. These values reflect the variability in OC and EC measurements that might be expected across laboratories.

Some source samples which were difficult to analyze because of recovery or pyrolysis problems showed much higher variability. For OC the catalyst equipped Buick and diesel Olds emissions and the soot sample showed the highest variability. But even for these samples most labs were still reasonably consistent. Supplying replicate source samples for the source samples and for the ambient samples would have aided in eliminating gross errors and potential sample non-homogeneity as sources of observed differences.

For EC, the leaded Chevy and the two wood smoke samples showed the highest variability. EC measurements for the organic aerosol were highly variable but too small to be considered anything but random instrument errors. The reason for the EC differences for most other samples appears to be primarily in how various laboratories handle sample pyrolysis. This is apparent, if we examine the wood smoke sample results. These samples contain a large OC component which will readily pyrolyze. DRI, GM and OGI seem to obtain reasonably good agreement on these samples. It would be expected that DRI and OGI agree because they use similar systems. Since GM agrees generally with DRI/OGI, it shows the possibility of obtaining agreement between thermo-optical and thermal systems. For the wood smoke samples, EC differences among all laboratories are large.

Figures III-2 and III-3 show matrix scatter plots for OC and EC data plotted in pairs. These figures show the general behavior of the data. The OC data plots show better correlation than the EC data plots.

Tables III-10 and III-11 show the OC and EC values from each laboratory ratioed against the average of all "consistent" laboratories for each sample. These values
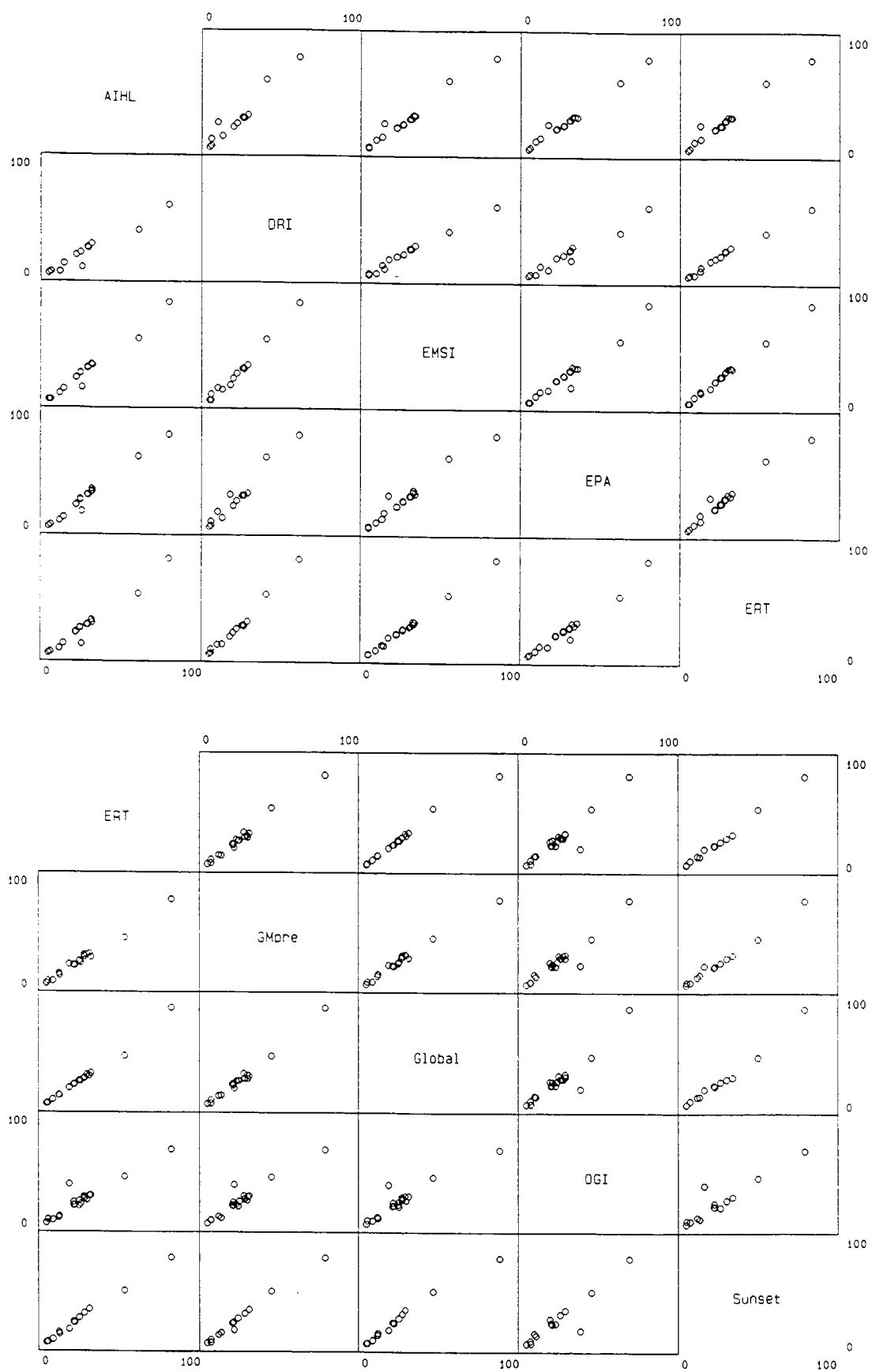
Figure III-2. Scatterplot Matrix for Organic Carbon (μg/cm^2) Data for Selected
Laboratories

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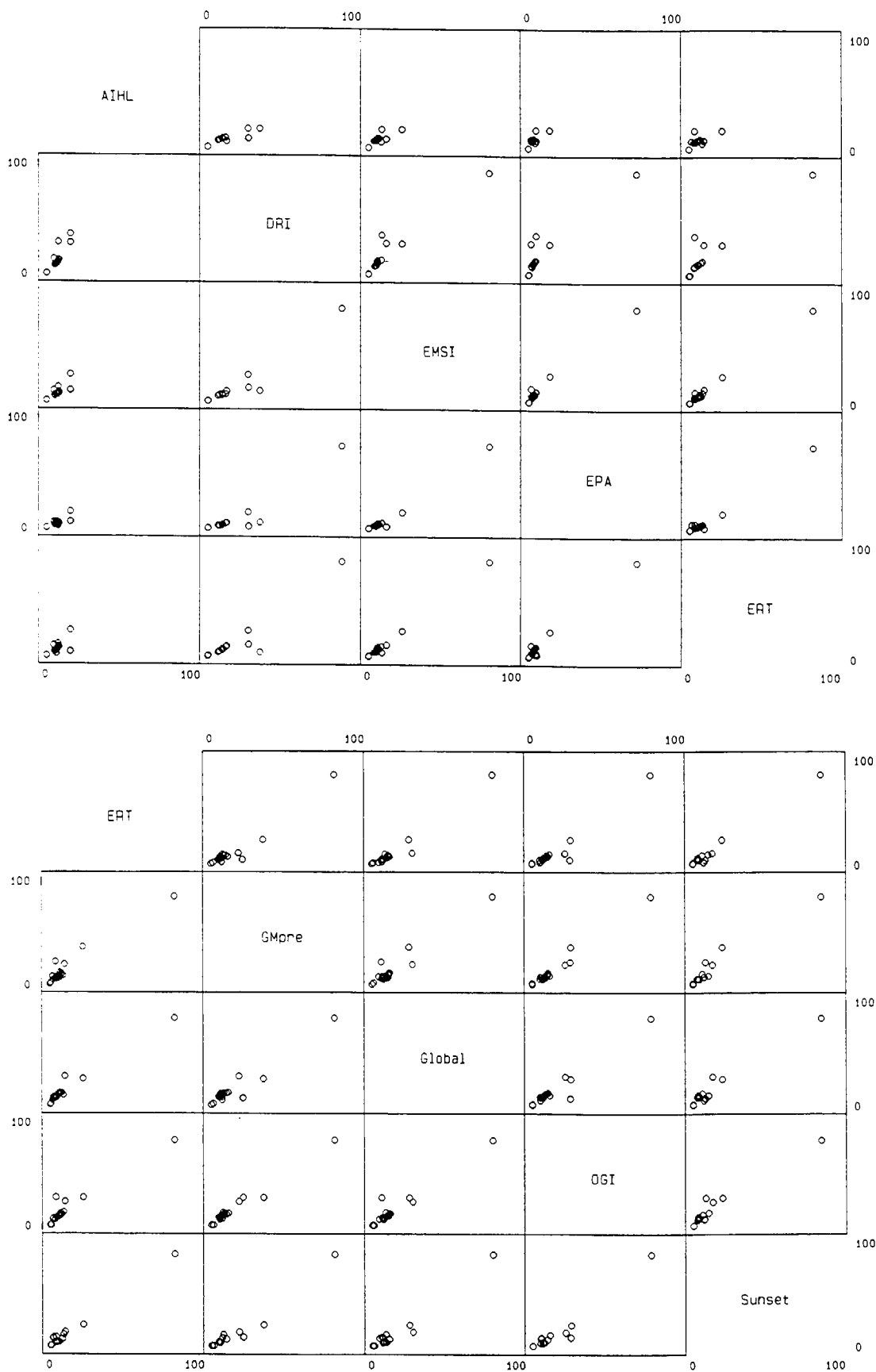Figure III-3.   Scatterplot Matrix for Elemental Carbon (μg/cm^2) Data for Selected
Laboratories

Table III-10. Ratios of OC Values for the Indicated Laboratories to the Average Sample OC Values

SAMPLE	TYPE	AIHL	DRI	EMSI	EPA	ERT	GM (Un)	GM (Pre)	Global	OGI	Sunset
01	Day 86	1.02	0.91	1.11	1.05	1.01	0.92	1.00	0.93	0.93	1.11
10	Day 86	1.07		1.12	1.15	0.98	0.90	0.99	0.99	0.80	
16	Day 86	1.02		1.07	1.16	1.05	0.89	0.87	1.01	0.93	
03	Night 87	1.01	0.90	1.08	1.07	1.04	0.90	0.93	1.05	0.97	1.05
05	Night 87	1.00		1.06	1.05	1.00	0.95	0.98	0.97	0.92	1.08
14	Night 87	0.99		1.05	1.02	0.99	0.88	0.95	0.99	1.09	1.05
06	Day 96	1.05	0.88	1.12	1.10	1.00	0.89	1.00	0.96	0.91	1.09
17	Day 96	1.02	0.91	1.09	1.10	0.97	0.96	1.06	0.92	0.98	
20	Day 96	1.03	0.91	1.14	1.12	1.01	0.89	0.99	0.95	0.95	
02	Night 97	1.02	0.88	1.13	1.12	1.04	0.87	1.00	1.05	0.77	1.12
04	Night 97	0.98		1.07	1.11	1.01	0.86	0.99	1.02	0.96	
08	Night 97	1.00		1.10	1.13	1.08	0.90	0.92	1.02	0.85	
Ambient	Avg.	1.02	0.90	1.09	1.10	1.02	0.90	0.97	0.99	0.92	1.08
	Std.	0.02	0.01	0.03	0.04	0.03	0.03	0.05	0.04	0.08	0.03
	CV%	2.29	1.55	2.68	3.74	3.01	3.06	4.85	4.12	8.84	2.46
07	Cat. Buick	2.13	0.52	1.03	1.30	0.80	1.10	0.90	0.78	0.52	0.91
11	Diesel Olds		0.73	0.72	1.52	0.80	0.92	0.96	0.79	1.93	0.64
18	Pb Chevy	1.24	0.80	1.12	1.28	1.08	0.75	0.90	0.93	0.91	1.00
12	Soot	2.00	0.32	1.44	1.33	1.15	0.45	0.67	1.09	0.77	0.77
19	Org. Aeros.	1.21	1.06	1.14	0.98	1.05	0.96	0.93	0.93	0.80	0.94
13	Wood Smoke	1.02	0.77	1.10	1.03	1.06	0.93	1.02	1.15	0.89	1.02
15	Wood Smoke		0.75	1.09	0.77	1.08	1.13	1.16	1.17	0.89	0.95
Source	Avg.	1.52	0.71	1.09	1.17	1.00	0.89	0.93	0.98	0.96	0.89
	Std.	0.45	0.21	0.20	0.24	0.13	0.22	0.14	0.15	0.42	0.13
	CV%	29.71	30.30	18.01	20.27	13.30	24.14	14.81	15.44	43.30	14.10
09	Blank	0.90	0.83	0.00	0.83	0.69	1.74	1.74	0.49	2.36	0.42

CV% = Coefficient of Variation = (Avg./Std.)x100

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Table III–11. Ratios of the EC Values for the Indicated Laboratories to the Average EC Sample Values

SAMPLE	TYPE	AIHL	DRI	EMSI	EPA	ERT	GM (Un)	GM (Pre)	Global	LBL	OGI	Sunset
01	Day 86	0.95	1.37	0.68	0.49	0.92	1.40	1.14	1.28	0.89	1.17	0.71
10	Day 86	1.02		0.79	0.46	0.92	1.33	1.02	1.33	0.86	1.27	
16	Day 86	0.96		0.83	0.45	0.79	1.21	1.30	1.35	0.86	1.25	
03	Night 87	1.13	1.40	0.86	0.52	0.72	1.19	1.07	1.54	0.97	1.03	0.58
05	Night 87	1.15		0.82	0.50	0.90	1.24	1.15	1.36	0.96	1.34	0.59
14	Night 87	1.15		0.78	0.51	0.84	1.29	1.02	1.33	1.02	1.43	0.64
06	Day 96	1.10	1.43	0.89	0.50	0.89	1.27	0.88	1.42	0.88	1.21	0.54
17	Day 96	0.98	1.33	0.75	0.42	0.74	1.37	1.02	1.36	0.84	1.19	
20	Day 96	1.02	1.37	0.75	0.48	0.91	1.16	0.83	1.44	0.83	1.20	
02	Night 97	1.13	1.42	0.94	0.38	0.70	1.30	0.82	1.36	1.01	1.24	0.72
04	Night 97	1.19		0.88	0.30	0.79	1.32	0.81	1.40	1.02	1.30	
Ambient	Avg.	1.07	1.39	0.82	0.45	0.83	1.28	1.00	1.38	0.92	1.24	0.63
	Std.	0.08	0.03	0.07	0.06	0.08	0.07	0.15	0.07	0.07	0.10	0.06
	CV%	7.70	2.37	8.56	14.09	9.75	5.62	15.00	4.75	7.63	7.82	10.26
08	Night 97	1.14		0.93	0.33	0.66	1.21	1.17	1.24	1.03	1.29	
07	Cat. Buick	0.70	1.18	1.00	0.63	0.98	1.44	1.53	1.08	0.48	1.14	0.86
11	Diesel Old	0.00	1.19	1.08	0.97	1.10	1.10	1.09	1.08	0.20	1.06	1.14
18	Pb Chevy	0.50	1.76	0.76	0.11	0.65	1.66	1.19	1.74	0.36	1.43	0.84
12	Soot	0.60	1.52	1.05	0.59	1.08	1.06	0.96	1.08	0.38	1.42	1.26
19	Org. Aeros	0.00	0.85	0.43	1.06	1.70	2.06	2.77	2.13	0.00	0.00	0.00
13	Wood Smo	1.05	2.27	0.58	0.34	0.24	1.81	1.38	0.41	0.71	1.69	0.53
15	Wood Smo	0.00	1.60	0.36	1.66	0.03	1.87	1.68	0.25	0.26	2.03	0.25
Source	Avg.	0.50	1.48	0.77	0.71	0.81	1.53	1.47	1.13	0.43	1.26	0.70
	Std.	0.43	0.43	0.27	0.47	0.49	0.36	0.54	0.58	0.30	0.56	0.43
	CV%	87.11	28.95	34.64	66.19	61.31	23.35	36.43	51.29	69.89	44.24	61.10
09	Blank	0.00	6.00	0.00	4.00	0.40	0.00	0.00	-1.00	0.00	0.00	1.60

should be similar for all samples analyzed by a given laboratory. When large differences occur for a particular sample analyzed by a given laboratory it may show that laboratory had difficulty dealing with that particular sample. Since true OC values are not known and there is no agreement on what true OC values are, noting that a laboratory's results are different does not show that they are wrong. One can only discuss why the differences may exist.

Since the analysis of ambient OC data yield the most consistent results these data were examined to determine how consistent OC data can be. Tables III-12 and III-13 show a summary of the ambient OC and EC data. Data precision ranged from under 1% to over 7% for both OC and EC. Values in the 2-3% range seem to be achievable for most laboratories for most of the samples. This would imply that if the analytical definitions of OC and EC were agreed upon and calibration standards were developed, OC and EC data as accurate and precise as TC data could be measured.

Tables III-14 and III-15 show the ambient OC and EC data range. The CV values show that OC consistency among laboratories is within 10%. However, for EC, CV values among laboratories are only within 30%. The larger data scatter for EC data, as compared to OC data, is probably results because the samples used in this study had smaller EC than OC mass fractions.

Tables III-16 and III-17 show ambient OC and EC results in magnitude order. Since most labratories obtained close agreement on TC data, those lababoratories which measured high OC values will also measure low EC values and vice versa. This is shown by comparing Tables III-16 and III-17. Regarding OC, the thermo-optical reflectance results (DRI and OGI) are significantly different from and are on the opposite ends of the data range from the thermo-optical transmission results (Sunset). It might have been expected that all thermo-optical systems would give similar results, because they are based on similar principles. Since this is not the case, the reasons for this difference needs to be resolved. This could be most effectively done using a thermo-optical carbon analysis system which was capable of doing the OC pyrolysis correction either by using reflectance and transmission. It is also necessary to

Table III-12. Summary of Ambient OC Data for Three Replicates (ug/cm2)

	AIHL	DRI	EMSI	EPA	ERT	GM (Un)	GM (Pre)	Global	OGI	Sunset	Avg. All Labs
Day 86											
Avg.	29.87	26.70	31.73	32.40	29.30	26.10	27.50	28.23	25.70	32.40	28.99
Std.	0.17		0.48	1.35	1.23	0.62	1.58	1.01	2.26		2.43
CV%	0.57		1.51	4.16	4.21	2.36	5.73	3.57	8.80		8.37
Night87											
Avg.	18.70	16.50	19.87	19.53	18.90	16.97	17.80	18.70	18.57	19.80	18.53
Std.	0.16		0.05	0.25	0.22	0.66	0.54	0.45	1.39	0.37	1.08
CV%	0.87		0.24	1.28	1.14	3.89	3.01	2.43	7.48	1.89	5.84
Day 96											
Avg.	27.03	23.67	29.27	29.00	25.97	23.93	26.60	24.73	24.80	28.40	26.34
Std	0.19	0.50	0.41	0.28	0.29	0.97	0.99	0.21	0.90		1.96
CV%	0.70	2.11	1.40	0.98	1.10	4.04	3.72	0.83	3.62		7.45
Night97											
Avg.	21.93	19.00	24.13	24.57	22.90	19.27	21.27	22.57	18.93	24.10	21.87
Std.	0.05		0.19	0.29	0.43	0.42	0.95	0.29	2.10		2.07
CV%	0.21		0.78	1.17	1.89	2.17	4.48	1.27	11.12		9.47

Where no Std. and CV values are shown the Avg. is the value of a single measurement.

Average of above Values

	AIHL	DRI	EMSI	EPA	ERT	GM (Un)	GM (Pre)	Global	OGI	Sunset	Avg. All Labs
Avg.	24.38	21.47	26.25	26.38	24.27	21.57	23.29	23.56	22.00	26.18	23.93
Std.	0.14		0.28	0.54	0.54	0.67	1.01	0.49	1.66		1.89
CV%	0.58		1.07	2.06	2.23	3.09	4.35	2.07	7.56		7.88

CV% = Coefficient of Variation = (Avg./Std.)x100

Table III-13.   Summary of Ambient EC Data for Three Replicates (ug/cm2)

	AIHL	DRI	EMSI	EPA	ERT	GM (Un)	GM (Pre)	Global	LBL	OGI	Sunset	Avg All Labs
Day 86												
Avg.	8.6	12.2	6.7	4.1	7.7	11.5	10.1	11.6	7.6	10.8	6.3	8.83
Std.	0.1		0.5	0.2	0.5	0.7	1.1	0.3	0.2	0.3		2.48
CV%	1.1		7.9	5.3	6.5	6.5	11.3	2.7	3.2	2.7		28.06
Night87												
Avg.	5.9	7.2	4.2	2.6	4.2	6.4	5.6	7.3	5.1	6.5	3.1	5.29
Std.	0.1		0.2	0.0	0.4	0.2	0.3	0.5	0.1	0.9	0.1	1.50
CV%	1.4		4.0	1.8	9.7	3.4	5.9	6.4	1.9	13.5	4.0	28.38
Day 96												
Avg.	7.5	10.1	5.8	3.4	6.2	9.3	6.7	10.3	6.2	8.8	3.7	7.10
Std.	0.1	0.2	0.2	0.2	0.5	0.8	0.7	0.5	0.2	0.4		2.25
CV%	1.7	2.4	3.2	4.8	8.6	8.4	11.1	4.8	2.7	4.0		31.72
Night97												
Avg.	6.8	8.3	5.4	2.0	4.2	7.5	5.5	7.8	6.0	7.5	4.2	5.92
Std.	0.1		0.3	0.2	0.2	0.1	1.1	0.2	0.2	0.2		1.83
CV%	1.8		4.9	10.4	5.1	1.7	20.6	3.0	2.8	2.9		30.99
Averages of Above Values												
Avg.	7.19	9.45	5.54	3.03	5.58	8.67	6.97	9.24	6.22	8.40	4.33	6.78
Std.	0.11	0.06	0.29	0.16	0.42	0.47	0.84	0.37	0.17	0.43	0.03	1.98
CV%	1.50	0.61	5.01	5.58	7.50	4.98	12.24	4.21	2.66	5.77	1.00	29.14

CV% = Coefficient of Variation = (Avg/Std.)*100

Table III-14. Range of Ambient OC Data* (ug/cm2)

	Max	Min	Avg.	Std.	CV%
Day 86	32.40	25.70	28.99	2.43	8.37
Night87	19.87	16.50	18.53	1.08	5.84
Day 96	29.27	23.67	26.34	1.96	7.45
Night97	24.57	18.93	21.87	2.07	9.47

CV% = Coefficient of Variation = (Avg/Std.)x100
*Includes: AIHL, DRI, EMSI, EPA, ERT, GM, Global, OGI, and Sunset.

Table III-15. Range of Ambient EC Data (ug/cm2)*

	Max.	Min	Ave.	Std.	CV%
Day 86	12.20	4.10	8.83	2.48	28.06
Night87	7.27	2.63	5.29	1.50	28.38
Day 96	10.30	3.40	7.10	2.25	31.72
Night97	8.30	1.97	5.92	1.83	30.99

CV% = Coefficient of Variation = (Avg/Std.)x100
*Includes: AIHL, DRI, EMSI, EPA, ERT, GM, Global, OGI, Sunset.

Table III–16. Sorted Average Ambient OC Data (ug/cm2)

Day 86		Night87		Day 96		Night97		Avg. of All Days	
OGI	25.70	DRI	16.50	DRI	23.67	OGI	18.93	DRI	21.47
GM-un	26.10	GM-un	16.97	GM-un	23.93	DRI	19.00	GM-un	21.57
DRI	26.70	GM-pre	17.80	Global	24.73	GM-un	19.27	OGI	22.00
GM-pre	27.50	OGI	18.57	OGI	24.80	GM-pre	21.27	GM-pre	23.29
Global	28.23	Global	18.70	ERT	25.97	AIHL	21.93	Global	23.56
ERT	29.30	AIHL	18.70	GM-pre	26.60	Global	22.57	ERT	24.27
AIHL	29.87	ERT	18.90	AIHL	27.03	ERT	22.90	AIHL	24.38
EMSI	31.73	EPA	19.53	Sunset	28.40	Sunset	24.10	Sunset	26.18
EPA	32.40	Sunset	19.80	EPA	29.00	EMSI	24.13	EMSI	26.25
Sunset	32.40	EMSI	19.87	EMSI	29.27	EPA	24.57	EPA	26.38

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Table III–17: Sorted Average Ambient EC Data (ug/cm2)

Day 86		Night87		Day 96		Night97		Avg. of All Days	
EPA	4.1	EPA	2.6	EPA	3.4	EPA	2.0	EPA	3.03
Sunset	6.3	Sunset	3.1	Sunset	3.7	ERT	4.2	Sunset	4.33
EMSI	6.7	ERT	4.2	EMSI	5.8	Sunset	4.2	EMSI	5.54
LBL	7.6	EMSI	4.2	ERT	6.2	EMSI	5.4	ERT	5.58
ERT	7.7	LBL	5.1	LBL	6.2	GM–pre	5.5	LBL	6.22
AIHL	8.6	GM–pre	5.6	GM–pre	6.7	LBL	6.0	GM–pre	6.97
GM–pre	10.1	AIHL	5.9	AIHL	7.5	AIHL	6.8	AIHL	7.19
OGI	10.8	GM–un	6.4	OGI	8.8	GM–un	7.5	OGI	8.40
GM–un	11.5	OGI	6.5	GM–un	9.3	OGI	7.5	GM–un	8.67
Global	11.6	DRI	7.2	DRI	10.1	Global	7.8	Global	9.24
DRI	12.2	Global	7.3	Global	10.3	DRI	8.3	DRI	9.45

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determine if the thermo-optical pyrolysis correction is dependent on aerosol type.

The perturbing effects of the addition of colored particulate material and the effects of the pyrolysis of adsorbed vapor OC on filters also need to be examined. One would expect that thermo-optical systems would measure higher OC values than thermal systems because thermal systems would count some OC as EC. Conversely, thermo-optical systems should measure lower EC than thermal systems. Based on the above rationale, Sunset results are of the correct magnitude compared to thermal method results. Considering ambient OC values, the Sunset values are probably at the higher end of the range in which the true values are to be found. Where to place the lower end of this range is a matter for speculation. All thermal system OC results, except for the EPA and EMSI, fall between the DRI and Sunset results. Interestingly, thermo-optical reflectance and thermo-optical transmission results bound most of the thermal system results. Thermal system results fall where they are expected to fall compared to at least transmission thermo-optical systems. All average ambient EC values, except those from the EPA laboratory, fall between the Sunset and DRI values.

Sunset, which uses a laser transmission measurement to do the pyrolysis correction, consistently obtained lower EC values than either OGI or DRI. This suggests that in a transmission system more carbon leaves the sample before the laser signal indicates that the sample has returned to its initial transmittance than must leave the sample to achieve initial reflectance in a laser reflectance system. Viewed from another perspective, the filter whitens faster in a reflectance system than it does in the transmission system; i.e., the measurement of EC starts sooner in a reflectance system analysis cycle and therefore if all other considerations are equal more EC is measured by the reflectance system. In the reflectance system, the laser beam interacts primarily with the surface of the filter where most of the particulate material is located. In contrast, in a transmission system, the laser interacts both with the surface of the filter and the whole body of the filter. Pyrolysis of adsorbed vapors within the body of the filter may therefore be more influential in a transmission system. It would seem that the determination of which system more correctly evaluates EC can be done only by some careful evaluation of appropriate external

standards. Research needs to be done to determine how thermo-optical and thermal system OC and EC results compare as a function of variations in the sample heating profiles and carrier gas compositions for samples with widely differing characteristics. Since no suitable combined OC and EC standards have yet been prepared, further research is necessary to resolve these problems.

Finally, differences in analysis results may involve how the analytical system handles carbonates. Sunset Laboratory measured 2 $\mu g/cm^2$ of carbonate in the automotive samples and in the wood smoke samples.

3.   Statistical Analysis of 1986 CSMCS

The Wilcoxon signed rank test is a non-parametric test which can be used to determine if two groups of data are drawn from the same population or different populations. This test was used to determine if the carbon analysis results from two laboratories are statistically similar or different. The test result is a z parameter which is normally distributed. Thus the results from two laboratories are statistically different, at the 95% confidence level, if $z \pm 1.97$ and at the 99% confidence level if $Z > \pm 2.58$.

Table III-18 shows z scores for TC results for all samples (n = 11 to 19) from all laboratories. While the best case (ambient samples) TC results showed that most laboratories were within 5% of the group average, the z scores show that over all samples many laboratory pairs produce statistically different results. Table III-19 shows z scores for OC results, and Table III-20 shows z scores for EC for all samples. These data confirm that interlaboratory OC and EC differences among laboratories are greater than those for TC. This occurs because OC and EC differences among laboratories are strongly related to the OC/EC split point determination.

B.   Interlaboratory Intercomparison Studies

Other formal and informal interlaboratory comparisons have been made over the past decade. In 1982 GM sponsored an intercomparison study where eleven

Table III-18. Wilcoxon z Scores for Total Carbon

	AIHL	COUL	DRI	EMSI	EPA	ERT	GM	GLOBAL	OGI	DEQ	SUNSET
AIHL	0.00										
COUL	-1.78	0.00									
DRI	-2.43	0.62	0.00								
EMSI	-1.00	1.01	2.20	0.00							
EPA	-3.83	-.59	-2.34	-3.14	0.00						
ERT	-3.66	0.35	-2.20	-3.17	1.67	0.00					
GM	-1.53	1.50	-0.10	-0.60	1.97	1.04	0.00				
GLOBAL	1.77	2.20	1.88	2.64	3.17	3.46	0.95	0.00			
OGI	-1.85	1.36	-0.14	-0.97	2.54	2.01	-0.30	-2.37	0.00		
DEQ	-3.82	-3.11	-3.18	-3.82	-3.82	-3.82	-3.82	-3.82	-3.82	0.00	
SUNSET	-2.83	0.35	-1.69	-2.52	0.77	-0.62	-1.64	-2.62	-1.92	3.18	0.00

Table III-19. Wilcoxon z Scores for Organic Carbon

	AIHL	COUL	DRI	EMSI	EPA	ERT	GM	GLOBAL	OGI	DEQ	SUNSET
AIHL	0.00										
COUL	-1.92	0.00									
DRI	-3.06	1.10	0.00								
EMSI	-1.55	1.91	3.04	0.00							
EPA	1.89	1.73	3.11	0.35	0.00						
ERT	-1.18	1.47	3.11	-3.32	-2.61	0.00					
GM	-3.63	-0.28	1.60	-2.69	-3.10	-2.35	0.00				
GLOBAL	2.94	0.80	3.17	-2.31	-3.06	-1.23	3.10	0.00			
OGI	-1.98	1.41	-0.14	-2.76	-2.39	-2.53	-2.03	2.46	0.00		
DEQ	2.42	2.17	2.86	2.80	2.20	3.14	3.00	2.56	2.43	0.00	
SUNSET	-0.39	1.22	2.59	-2.62	-1.16	-0.53	1.32	1.16	0.60	-3.10	0.00

Table III-20. Wilcoxon z Scores for Elemental Carbon

	AIHL	COUL	DRI	EMSI	EPA	ERT	GM	GLOBAL	OGI	DEQ	SUNSET
AIHL	0.00										
COUL	1.29	0.00									
DRI	3.06	1.88	0.00								
EMSI	-1.44	-2.04	-3.30	0.00							
EPA	-3.51	-2.20	-3.04	-3.06	0.00						
ERT	-1.50	-2.92	-3.17	-3.17	1.67	0.00					
GM	3.62	1.22	-1.22	3.82	3.88	3.62	0.00				
GLOBAL	1.19	0.03	-1.91	3.26	3.88	2.89	-3.12	0.00			
OGI	2.94	0.62	-1.85	2.83	3.14	3.66	0.44	1.45	0.00		
DEQ	-3.46	-3.23	-2.91	-3.29	-2.63	-3.21	-3.70	-3.49	-3.70	0.00	
SUNSET	-0.53	-2.55	-3.06	-1.22	2.07	0.34	-2.79	-2.26	-2.10	3.10	0.00

laboratories analyzed three ambient samples (Cadle et al., 1983). The differences in determining total carbon (TC) varied so much among laboratories that an intercomparison of OC and EC results was not feasible.

1.   1989 OMNI/DRI Carbon Intercomparison Study

In 1989, OMNI, in cooperation with DRI, completed a study for ARB to determine Chemical Mass Balance (CMB) source profiles for the California Great Basin Valleys, San Joaquin Valley and the Southeast Desert Basins (Houck et al.,1989). In this study, a set of 20 soil, road dust, fireplace, wood stove, diesel bus, field burning, construction dust, dairy dust, and crude oil burning emission samples were sent to DRI, Sunset and ENSR for interlaboratory carbon analysis. Table III-21 shows the results of this study.

As in previous intercomparison studies, each laboratory calibrated against its own standards. To obtain a measure of each laboratory's performance OC, EC, and TC values for each laboratory were summed for all samples. The TC sum ranking from low to high is ENSR, DRI, and Sunset. DRI and Sunset were nearly identical and ENSR was lower than DRI and Sunset. The TC differences are of the order of 5% which is similar to other intercomparison studies. Ranking OC sums shows ENSR is low, DRI is middle, and Sunset is high. Ranking EC sums would have reversed the OC rank order, except since ENSR is low for TC, ENSR and DRI exchange positions, making DRI high. OC and EC data determined by DRI and ENSR might be considered very similar for this data set. However, in the 1986 intercomparison study, ENSR (ERT) agreed better with Sunset laboratory than with DRI. This shows that different OC and EC values may be obtained either when samples are analyzed at different times by a single laboratory or when they are analyzed by different analytical systems.

As in other intercomparisons, the two thermo-optical methods differ significantly while the thermal method gives results falling between the two thermo-optical methods. This intercomparison study does not resolve the question of which OC and EC analytical system best determines the OC/EC split. Based on these data, all three systems obtain somewhat different results. The question of which method is

Table III-21. Results of the OMNI/DRI Carbon Intercomparison Study (ug/cm2)

	OC				EC				TC=OC+EC			
	DRI	Sunset	ENSR	CV%	DRI	Sunset	ENSR	CV%	DRI	Sunset	ENSR	CV%
1	1.5	0.7	0.5	47.3	0.1	0.2	0.3	51.0	1.6	0.9	0.8	32.1
2	21.0	24.5	17.9	12.7	5.4	3.0	3.5	26.3	26.4	27.4	21.4	10.5
3	18.2	21.5	14.8	15.1	1.6	1.3	3.5	46.9	19.8	22.8	18.3	9.2
4	22.4	25.2	24.3	4.9	3.8	1.7	5.4	41.2	26.2	26.9	29.7	5.5
5	4.3	2.5	3.6	22.1	0.0	0.1	0.3	88.1	4.3	2.6	3.9	20.7
6	3.9	4.4	3.3	11.5	0.1	0.1	0.3	42.4	4.0	4.5	3.6	9.6
7	20.0	21.9	17.9	8.2	1.5	1.0	0.4	48.7	21.5	22.9	18.3	9.2
8	2.3	2.7	2.7	6.6	0.1	0.1	0.3	38.8	2.5	2.8	3.0	7.4
9	2.9	2.6	2.8	5.7	0.0	0.1	0.3	88.1	2.9	2.7	3.1	5.8
10	5.1	3.7	13.7	58.9	0.0	0.1	1.0	122.6	5.1	3.8	14.7	61.8
11	25.6	26.8	21.9	8.4	5.2	2.3	4.6	31.1	30.8	29.1	26.5	6.1
12	92.9	101.5	91.1	4.7	37.7	27.3	27.2	16.0	130.6	128.7	118.3	4.3
13	171.9	245.0	263.3	17.4	54.4	24.3	57.1	32.9	226.3	269.3	320.4	14.1
14	114.5	138.0	107.7	10.8	3.0	0.1	5.8	78.9	117.4	138.1	113.5	8.8
15	25.1	29.1	21.2	12.8	2.7	0.8	4.1	54.0	27.9	29.8	25.3	6.7
16	39.9	47.9	38.5	9.9	14.7	6.1	6.8	42.3	54.6	54.0	45.3	8.3
17	7.2	4.9	5.6	16.3	2.4	1.8	2.3	13.3	9.6	6.6	7.9	15.1
18	8.6	9.7	8.7	5.2	2.2	0.9	2.2	34.5	10.8	10.6	10.9	1.3
19	26.2	29.5	24.3	8.0	24.5	19.2	17.5	14.6	50.7	48.7	41.8	8.1
20	24.1	30.0	23.1	11.8	17.8	8.5	15.4	28.6	41.9	38.4	38.5	4.1
Avg.				14.9				47.0				12.4
Sum*	465.7	526.8	443.6		122.6	74.5	100.9		588.3	601.2	544.5	
Avg. of sums	478.7				99.3				578.0			
Std. of sums	35.2				19.7				24.3			
CV% of sums	7.4				19.8				4.2			

*Excludes sample #13

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preferred still needs to be resolved.

The averages, standard deviations and coefficients of variation, for the sample sums for OC, EC, and TC data are shown at the bottom of the table. The coefficients of variation for OC, EC, and TC sums are 7.3%, 19.3%, and 4.2%, respectively. These coefficients might be considered to be estimates of the standard error of the mean that might be expected for intercomparisons of these laboratories. As with previous intercomparison studies, the agreement in the determination of TC is within 5%. Agreement on OC and EC values is poorer but similar to results obtained in previous intercomparisons. If one accepts that air pollution data would be expected to be accurate within 10%, then this EC data would be unacceptable. As with previous intercomparison studies, there is no way to determine laboratory accuracy or preferability.

IV. STRATEGIES TO RESOLVE OC AND EC DIFFERENCES

This section presents and discusses three topics: 1) questions to be resolved in OC and EC analysis; 2) preparation of standards; and, 3) experiments to be done.

A.   Questions To Be Resolved in OC and EC Analysis

OC and EC source and ambient particulate data are analysis method-dependent. There has been no well accepted agreement on preferred analysis method or on the specific parameters to be used with a given method. It is important to achieve consensus on the definition of OC and EC. The following are some specific questions to resolve in current OC and EC analysis.

1.   What are the sources of OC and EC differences among various analysis systems?

   a.   The highest temperature used for OC volatilization in current analysis methods ranges from 400 to 700°C. Research should determine the relative amount of OC that is volatilized in the 500 to perhaps 700°C range to determine a reasonable OC cutoff temperature.

   b.   The highest temperature to use for EC oxidation used for EC oxidation ranges from 600 to 950°C. Research should determine the highest temperature necessary to completely oxidize EC for particulate material from all major sources.

2.   What is the role of OC pyrolysis in both thermal and thermo-optical carbon analysis?

   a.   It is known that the pyrolytic conversion of OC to EC can occur during the heating phase used to volatilize OC in all thermal analysis methods. Current analysis methods either attempt to minimize this conversion or attempt to compensate for the

conversion. Research needs to be done to examine current analysis methods to determine if these methods correctly determine the OC/EC split. This will require the development of OC and EC standards which can then be tested on the various analytic systems.

b. The conditions under which various types of EC oxidize during OC analysis need to be determined. Some analysis systems attempt to suppress pyrolization by adding oxygen to the helium carrier stream during OC analysis. This may cause the appearance of lowering pyrolization, but this may be due to prompt oxidation of EC produced by pyrolization. Also trace amounts of oxygen may oxidize EC at temperatures as low as 300-400°C. Research needs to be done to examine EC oxidation during OC analysis.

3. The difference in OC and EC split point determination between thermo-optical reflectance and transmission systems needs to be resolved. Can accurate OC and EC values be determined for all ambient aerosols given some agreement on analysis temperatures to be used or must OC and EC values be analysis method-dependent? The role of vapor carbon species deposition throughout the filter body on the determination of the OC/EC split needs to be examined. The response of thermo-optical systems to colored aerosols also needs to be examined. This should include both the study of organic compounds which are black, for example tar, colored organic compounds such as aniline dyes, colored metallic oxides such as the iron and copper oxides that might be found near metal smelting operations.

Since thermal carbon analysis systems have no mechanism to accommodate pyrolysis correction for different types of aerosols it would seem that they will always require the appropriate thermal program adjustment to obtain the correct OC/EC split for the particular carbonaceous material being analyzed.

4. The analytical differences between thermo-optical reflectance and transmission systems need to be reconciled.

5. The role of carbonates in OC and EC analysis needs to be examined. This should include the examination of both simple carbonates and complex mineral carbonates under acidification and heating conditions.

B. Preparation of Standards

1. TC standards should be uniformly deposited on filters at various values of carbon deposit per unit area between 1 and 500 $\mu g/cm^2$. Quartz fiber filters should be used to eliminate the problems associated with the melting of glass fiber filters. These standards might be prepared by uniformly wetting a quartz filter fiber with a sucrose or KHP solution and determining the carbon deposit by weighing the dried filter before and after making the deposit. In systems that differentiate between OC and EC these standards should be detected as nearly 100% OC.

2. OC standards deposited on filters can be prepared by soaking quartz fiber filters in sucrose or KHP solutions and drying these filters in clean air. Standard deposition per unit area can then be determined by weighing the filter. Procedures must be developed to insure uniform standard deposition per unit area. The relation between standard solution concentration and dry standard deposit should be established. Standards that examine the high temperature volatilization behavior of difficult-to-volatilize OC compounds need to be developed to aid in the determination of a standardized upper temperature limit for OC analysis.

3. EC standards might be prepared by sampling air in which powdered charcoal has been dispersed. These standards should be heated to the maximum OC analysis temperature to remove OC contamination. These standards should be detected as nearly 100% EC. EC concentration per unit area should be uniform and determined both by weighing and

analysis for TC. EC standards might also be prepared by pyrolizing OC or using diesel emissions. Such standards must also be heat treated to remove OC contamination. EC standards may have to be heat treated before use to remove OC vapor deposition acquired during storage.

4. Combination OC and EC standards can be prepared by a combination of steps 1 and 2 above. An OC and EC analysis system should be able to correctly analyze such a standard. Since this has not yet been done, it needs to be tried to determine if the expected results are obtained. Using ambient samples to compare OC and EC analysis systems can only address relative differences and is not useful to determine if OC or EC are being determined accurately.

C. Experiments

1. Compare thermograms from different analysis procedures to look for similarities and differences.

2. Determine if pyrolyzed carbon has similar blackness in terms of change in laser interaction with the filter related to EC $\mu g/cm^2$.

3. OC and EC Split Experiment

Place a known amount of sucrose on a clean quartz filter in the boat. Run analysis to just before oxygen is added to carrier stream. Pyrolized carbon is now the initial sucrose minus what has been so far removed. Add a further known amount of sucrose. Analyze this sample as a normal sample. Both OC and EC are known for this sample.

4. More Intercomparison Studies

Until OC and EC standards have been developed, carefully planned interlaboratory comparison studies such as CSMCS should be conducted periodically to better understand differences among laboratories.

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VI. GLOSSARY

Carbonaceous Aerosol--Suspended particulate material which contains a carbon component.

Black Carbon--a common name for elemental carbon.

Elemental Carbon (EC)--a form of carbon which is essentially pure carbon rather than being chemically combined with hydrogen and/or oxygen. It can exist either in an amorphous or crystalline structure.

Free carbon--a common name for elemental carbon.

Graphitic carbon--a common name for elemental carbon.

Pyrolysis--The process by which organic carbon compounds lose hydrogen and/or oxygen at high temperatures and change their chemical structure to become elemental carbon.

Organic Carbon (OC)--any of the vast number of compounds where carbon is chemically combined with hydrogen.

Secondary atmospheric processes--processes in the atmosphere whereby vapor or gaseous species are transformed into the particle phase.

Soot--a common name for elemental carbon. It may be a misleading term because soot as found in chimneys often also contains an organic carbon component.

Total Carbon (TC)--The sum of all particulate carbon which is either in the form of organic carbon, elemental carbon or inorganic carbonate carbon.

Coefficient of Variation (CV)--standard deviation divided by the average. This shows the scatter around the average.

Organic Vapor Adsorption (OVA)--sampling artifact that occurs due to adsorption of organic vapors on the quartz or glass fiber filter material.

Carbonate Carbon (CC)--inorganic carbonate salts.

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APPENDIX A

LISTING OF THE
CARBONACEOUS SPECIES METHODS COMPARISON STUDY (CSMCS)
INTERLABORATORY ROUND ROBIN PARTICIPANTS

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APPENDIX B

DESCRIPTION OF CARBON ANALYSIS ANALYTICAL METHODS USED BY THE CARBONACEOUS SPECIES METHODS COMPARISON STUDY (CSMCS) INTERLABORATORY ROUND ROBIN PARTICIPANTS

Table of Contents

Organic and Elemental Carbon Analysis Methods

The following information was supplied by the participating laboratories. It should be noted that all laboratories did not supply measurement range, minimum detection limit, nominal TC accuracy and nominal OC, EC and TC precision information. It can be assumed that the missing data would be similar to that given by laboratories which did supply data.

1. Air and Industrial Hygiene Laboratory (AIHL)

Method: Thermal plus optical absorption

Sample: TC variable from 8-17 cm^2 of filter.
   EC 17 cm^2 (for convenience, actual beam size ca. 1 cm^2.)

Species Measured: TC and EC

Organic Carbon Analysis: OC = TC-EC

Elemental Carbon Analysis: Elemental carbon was assessed by measuring light absorption with quartz filter samples using a He-Ne laser (632.8 nm) absorption method first described by Rosen et al, 1978. This procedure may be considered a version of the integrating plated method, with the filter, itself, replacing the integrating plate to provide uniform intensity to all forward-scattered light. A large lens immediately behind the sample is used to focus the light onto the detector. The decrease in light intensity reaching the detector, relative to that for a blank filter, is assumed to be due to light absorption by the particulate matter sample. Furthermore, elemental carbon is assumed to be the only light-absorbing species present. Thus "black carbon" is equated with elemental carbon.

Total Carbon Analysis: Total carbon was determined with a Coulometrics Inc. Model 5010 coulometer and Model 5020 total carbon apparatus. In this technique the sample is combusted in oxygen with conversion to carbon dioxide aided by $BaCrO_4$. In the coulometer cell, the CO_2 is absorbed by an ethanolamine solution forming a titratable acid. In the automatic coulometric titration, the current generates a base which neutralizes the acid formed by the CO_2 and the result is electronically displayed on the coulometer as μg of carbon. Employing a combustion tube temperature of 1200°C, the accuracy of carbon analysis of potassium acid phthalate and graphite was >99% and 97%+-2%, respectively. To extend the heater block lifetime, the combustion tube temperature was reduced to 1100 °C midway during the analysis of atmospheric samples with no measurable decrease in accuracy with graphite. Under similar conditions, calcium carbonate gave 103-104% recovery of carbon, whereas sodium and potassium carbonates yielded recoveries ranging from 84 to

100%. The total carbon analysis is considered to provide the sum of OC, EC ("or black") carbon and carbonates in atmospheric samples. The very high temperature used in this analysis procedure should result in maximum measurements of TC

Carbonate Carbon Analysis: Carbonate was determined on a subset of hi-vol filter samples using the Model 5030 carbonate carbon apparatus in which samples are acidified and the evolved CO_2 transferred to the coulometer. With 110 to 210 μg $CaCO_3$ samples, the recovery of carbon was 84 +-2.9%. With Na_2CO_3, recovery averaged 94.8 +-1.9%.

Measurement range: EC: 1.5-15 μg/cm^2, TC >0.4 μg/cm^2.

Nominal Accuracy: EC: unknown, TC 1-5%.
Nominal Precision (for round robin data): EC < =3%, TC: < =2%

2. Coulometrics, Inc.

Analysis procedure is similar to Global Geochemistry. The use of a coulometer to measure CO_2 is described in the AIHL total carbon analysis procedure.

3. Desert Research Institute (DRI)

Method: Thermal Optical Reflectance

Sample: 0.503 cm^2 round disc.

Species Measured: OC, EC, TC=OC+EC, carbonate can be measured, as a separate analysis procedure, by acidifying the sample and recording the evolved CO_2 prior to doing the OC/EC analysis.

System Description: This system is a modified version of the OGI system. The DRI/OGI thermal/optical carbon analyzer is based on the preferential oxidation of organic and elemental carbon compounds at different temperatures. It relies on the fact that organic compounds can be volatilized from the sample deposit in a helium atmosphere at low temperatures, while elemental carbon is not oxidized and removed. The analyzer operates by: 1) liberating carbon compounds under different temperature and oxidation environments from a small punch (0.503 cm^2) taken from a quartz-fiber filter; 2) converting these compounds to carbon dioxide by passing the volatilized compounds through an oxidizer containing heated manganese dioxide; 3) reduction of CO_2 to methane by passing the flow through a methanator (hydrogen-enriched nickel catalyst); and 4)quantification of CH_4 equivalents by a flame ionization detector. The system is controlled by a personal computer which controls gas flows and sample oven temperatures during the analysis and processes data for display on a monitor

screen, for graphical plotting and for computer storage. Carbon from the sample is oxidized to CO_2 in a MnO_2 oxidation oven. CO_2 is reduced to CH_4 in a nickel catalyst on firebrick methanator and detected by a flame ionization detector. Conversion to CH_4 is required because the FID is highly sensitive to CH_4 and the FID has varying sensitivities to other carbon compounds. The constant temperatures in the MnO_2 oxidation oven and the methanator are maintained by temperature controllers. Gas flows to the sample oven and FID are controlled by: (1) a system of manually set rotameters and precision valves; and (2) a Carle electrically driven chromatography valve is used to inject a known volume of calibration gas for internal system calibration; and 3) two sets of 3-way solenoid valves (these replace two Carle Valves used in the OGI system).

The pyrolytic conversion correction system consists of a He/Ne laser, fiber optic light pipes, an optical quality quartz rod which is centered in the sample heating zone, a narrow band pass filter which discriminates against oven glow, and a photo-detector. Light from a He/Ne laser is conducted to the quartz rod by a fiber optic light pipe and illuminates the sample surface during the analysis procedure. Reflected laser light from the sample is conducted back down the quartz rod to a photo cell detector. The photo-detector signal is proportional to filter blackness.

Analysis Procedure: Samples are placed in a quartz boat which is moved into sample oven 120 seconds after the computer-controlled analysis program is started. The analysis proceeds automatically under computer control. Carbon detected by the FID, sample oven temperature, and laser reflectance signal are graphically displayed on a monitor. The laser signal starts at an initial value and decreases as organic material on the filter is pyrolytically converted (by charring) to elemental carbon. When O_2 is introduced the laser signal increases as the filter becomes more reflective, i. e., as EC is oxidized from the filter. All carbon that is removed from the filter after the point the filter blackness returns to its initial value is recorded as elemental carbon.

Organic Carbon Analysis: The sample is heated in an atmosphere of He at temperature steps of 250, 450, and 550°C to vaporize organic carbon. The step heating program is used to minimize pyrolytic conversion of organic carbon to elemental carbon. After the sample OC emission rate drops to a low value at 550°C, 2% O_2 is introduced into the carrier stream. OC that volatilizes at temperatures greater than 550C and above will be recorded as EC with this system. The endpoint of organic carbon analysis is determined by the point at which the filter returns to its initial blackness following the introduction of O_2 into the carrier stream. It is assumed that pyrolized organic carbon has the same light absorbance as the elemental carbon initially loading the filter. This system also compensates for elemental carbon that might be removed from the filter by trace amounts of O_2 in the filter deposit during OC analysis.

Elemental Carbon Analysis: EC analysis follows OC analysis. The measurement of initial EC starts after the filter has returned to its initial blackness after pyrolized organic carbon has been oxidized. The sample oven temperature is increased to 700°C and then to 800°C for elemental carbon analysis. EC measurement is concluded when the sample stops emitting carbon at 800°C. EC that does not oxidize at 800°C will not be detected by this system.

Total Carbon Analysis: TC = OC + EC

Measurement range: 0.2 - 750 μg/cm^2
Minimum detection limit: 0.2 μg/cm^2
Nominal Accuracy: TC: 5%.
Nominal Precision: OC: 5-10%   EC: 5-10%   TC: 4%
Carbonate Carbon Analysis Precision: 10%

4. Environmental Monitoring & Services, Inc. (EMSI)

Method: Thermal

Sample: 1/4 inch diameter punch (0.3137 cm^2)

Species Measured: OC and EC

System Description: The instrument used is a Dohrman Model DC-52C carbon analyzer equipped with a Horiba PIR 2000 non-dispersive infrared NDIR CO_2 detector

Organic Carbon Analysis: The sample is inserted through an inlet port into a platinum boat. The inlet port is then sealed and ultra high purity helium carrier gas (10 cc/min) is introduced into the system The sample boat is advanced to the vaporization zone where the sample is dried at a temperature of 110°C for two minutes. Next, the sample boat is advanced into a heated furnace zone at a temperature of 600°C for a period of five minutes. Organic compounds on the filter punch are volatilized (but not oxidized) and are transported downstream in the helium carrier gas to a zone packed with manganese dioxide (MnO_2) and heated to 350°C. Here the gaseous hydrocarbon species are converted to CO_2 which is then detected by the NDIR CO_2 detector. At the end of five minutes the sample boat is withdrawn from the furnace to cool down for one minute. The sample is then removed from the platinum boat and stored for elemental carbon determination.

Elemental Carbon Analysis: A sample which has been analyzed for OC is placed in the platinum sample boat and the inlet port is sealed. The sample boat is then advanced into a furnace zone heated to 750°C. The carrier gas used in this analysis contains 2% O_2 which oxidizes graphitic "elemental" carbon.

Total Carbon Analysis: TC = OC + EC

Carbonate Carbon Analysis: This analysis is not done as a separate analysis.

Standards: A 1800 ppm carbon stock aqueous solution of KHP is diluted with 0.1% phosphoric acid to 400 ppm carbon for medium range carbon analysis and to 180 ppm carbon for low range carbon analysis. A 50 μl syringe is used to inject calibration solutions into the analyzer.

Measurement range: 0.8-45 μg carbon.
Minimum detection limit: 0.3 μg/cm² per punch.

5. Environmental Protection Agency (EPA)

Method: Thermal

Sample: 0.665 cm diameter filter disc

Species Measured: OC (volatile carbon) + EC

System Description: This method has been described by Stevens, 1978. It is a combustion technique based on the use of a modified Dohrman DC 50 carbon analyzer. The heart of the instrument is a single quartz tube in which combustion and reduction of combustion gases occur. The combustion zone typically operates between 600°C and 650°C. A catalytic reduction zone containing a nickel-oxide-on-alumina catalyst is maintained at 300°C. A flow of hydrogen gas is fed into the front of the catalyst bed. The reduction zone is followed by an FID which is used to detect the amount of carbon. The carrier gas is either 100% helium or 2% oxygen in helium and is fed into the inlet of the tube. The 2% oxygen is used in the elemental carbon phase.

Organic Carbon Analysis: Initially a 0.665 cm filter disc is placed in a quartz sample boat inside the quartz tube. The boat is moved into the combustion zone which is at 600°C. The carrier gas is 100% helium. The combustion gases are reduced in the catalytic zone and them measured by FID. The measurement gives the volatile carbon. The measurement procedure does not take into account any charring which may take place in the volatile carbon phase.

Elemental Carbon Analysis: For elemental carbon measurement, the carrier gas is switched for 100% helium to 2% oxygen in helium and the temperature of the combustion zone is raised to 650°C. The sample is then returned to the combustion zone. As before the gases are reduced in the catalytic zone and then measured by the FID.

Carbonate Carbon Analysis: The method does not consider carbonate carbon.

Standards: Aqueous potassium hydrogen phthalate (KHP)

6. ERT (now AtmAA, Inc.)

Method: Thermal method with oxygen for EC oxidation supplied by heated MnO_2

Sample: 0.0702 cm^2 round disc

Species Measured: VOC, acid released carbon (ARC), residual organic carbon ROC, EC.

System Description: This system uses a Dohrmann DC-50 or DC-52-A instrument to oxidize carbonaceous particulate material sequentially at 525°C and 850°C in the presence of manganese dioxide to carbon dioxide. The Dohrmann instrument is controlled by an IBM compatible computer. It consists of two modules: the Totalizer module in the upper section, which houses the electronics, and the lower section which houses the reaction module where sample pyrolysis, reduction, and detection occur. The CO_2 is reduced by a hydrogen-enriched nickel catalyst at 350°C to methane (CH_4) for detection by a flame ionization detector (FID), which responds linearly to CH_4.

Analysis Procedure: A sample is placed into a platinum boat containing MnO_2. Gas flows are allowed to stabilize. The boat is manually inserted into the sample oven (vaporization zone). After VOC is released, the sample boat is returned to the injection port and 30 μl of acidified water is injected onto the sample. The auto loading system is then engaged and the sample analysis is completed under computer control for ARC, ROC and EC.

Organic Carbon Analysis: The sample is heated at 120°C to liberate volatile organic carbon (VOC). Then the sample is then acidified and reheated to 120°C. The carbonate (CO_3) and some organics (e. g., salts of low molecular weight fatty acids) released under these conditions are termed acid released carbon. Upon release, both of VOC and ARC are flushed to the nickel catalyst and reduced to CH_4 for detection. Residual organic carbon (ROC) is released by heating the sample to 525°C

Elemental Carbon Analysis: The sample is heated at 850°C until carbon emission from the sample stops. The OC/EC split is completely defined by the temperature steps used in the analysis.

Total Carbon Analysis: $TC = VOC + ARC + ROC + EC$

Carbonate Carbon Analysis: A maximum estimate of carbonate is given by ARC.

Standards: External potassium hydrogen phthalate. 360, 180 and 90 ppm carbon standards are used. System is calibrated once per day and also after the MnO_2 is changed.

Measurement range: OC 154 $\mu g/cm^2$, EC 154 $\mu g/cm^2$, TC 154 $\mu g/cm^2$.
Minimum detection limit: 0.15 $\mu g/cm^2$
Nominal Accuracy: OC: 2-5%   EC: 5-8%   TC: 2-5%
Nominal Precision: OC: 2-5%   EC: 5-8%   TC: 2-5%

7. General Motors Research Laboratory (GMR)

Method: Thermal

Sample: punch from filter

Species Measured: OC and EC

System Description: This is an automated system described by Cadle et al., 1983.

Analysis Procedure: Preheating sample to 350°C in air followed by heating the sample in helium to 950°C is believed to minimize charring.

Organic Carbon Analysis: Two Step Process: A filter punch is placed in a furnace at 650°C in a helium atmosphere. Volatilized carbon carried by a stream of helium is oxidized to CO_2 and then measured with a non-dispersive infrared CO_2 analyzer. Because no correction is made for pyrolized OC, carbon detected in this phase of the analysis is called "apparent OC".
    A four-step thermal process is also used which minimizes the measurement of original OC as EC due to pyrolysis. In this process one punch from the filter is analyzed for TC. A second punch is heated in air at 350°C for 10 minutes in a furnace in order to remove as much of the organic carbon as possible. This second piece is then analyzed using the pyrolysis-oxidation procedure to determine EC. Organic carbon is then determined by the difference (OC = TC-EC).

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Elemental Carbon Analysis: After the OC analysis, the carrier gas stream is changed to 350°C air to oxidize EC. This step is followed by a 950°C pyrolysis step. Since no correction for pyrolysis is made this carbon is called "apparent EC".

Total Carbon Analysis: $TC = EC + OC$

Standards: Calibration is performed by syringe injection of pure CO_2 and CH_4. Analyzer performance is monitored by automatically injecting a known volume of an NBS standard consisting of 0.95% CO_2 in N_2 after every sample.

8. Global Geochemistry Corp. (GGC)

Method: Thermal

Species Measured: OC and EC

Analysis Procedure: CO_2 measured by Coulometrics, Inc. electrochemical cell

Organic Carbon Analysis: Sample is heated to 400°C in an atmosphere of oxygen

Elemental Carbon Analysis: Sample is heated to 700°C in an atmosphere of oxygen.

Total Carbon Analysis: $TC = OC + EC$

Carbonate Carbon Analysis: Not measured

9. Lawrence Berkeley Laboratory (LBL)

Method: Optical absorption measurement of EC. Real time measurement with aethalometer instrument developed at Lawrence Berkeley Laboratory (Hansen and Novakov, 1990).

Sample: Filter collection spot area = 1.14 cm^2.

Species Measured: EC

System Description: The aethalometer continuously measures the reduction of transmitted light (incandescent lamp) intensity through a spot on a filter which is continuously collecting ambient aerosol. The change of light transmission intensity per unit time is proportional to the amount of light absorbing black carbon (EC) that is collected over that period of time. The sampling air flow rate is 4-8 L/min. Usually filters are changed every 6 hours in air where the EC concentration ranges from 2-5 $\mu g/m^3$. Air flow rate is monitored by a mass flow meter.

Organic Carbon Analysis: Not measured

Elemental Carbon Analysis: Optical absorption

Total Carbon Analysis: Not measured

Carbonate Carbon Analysis: Not measured

10. Oregon Department of Environmental Quality

Method: Thermal
Species Measured: TC and OC
System Description: System and analysis procedure is similar to EMSI

11. Oregon Graduate Institute (OGI)

Method: Thermal Optical Reflectance (Huntzicker et al., 1982)

Sample size: 0.25 cm^2 round disc. Usually 4 discs are used per analysis.

Species Measured: OC, EC, TC = OC + EC, carbonate can be measured in a separate instrument.

System Description: The system consists of a temperature controlled sample heating oven followed by a carbon oxidation oven and a methanator which converts CO_2 to CH_4. CH_4 is detected by a flame ionization detector. The system temperatures and gas flows are controlled Commodore 64 computer. The computer also processes data for display on a monitor screen, for graphical plotting and for computer storage. The carbon oxidation oven converts all carbon compounds to CO_2 by oxidation over a MnO_2 catalyst. The methanator reduces CO_2 CH_4 over a nickel catalyst on firebrick. Conversion to CH_4 is required because the FID is highly sensitive to CH_4 and the FID has varying sensitivities to other carbon compounds. The constant temperatures in the MnO_2 oxidation oven and the methanator are maintained by temperature controllers. Gas flows to the sample oven and oven are controlled by (1) a system of manually set rotameter and precision valves, and (2) three multi-port electrically driven Carle chromatography valves. The carrier gas stream is composed of three components: the main helium stream, a 10% O_2 90% He stream, and a stream of He equal in flow rate to the 10% O_2 90% stream. The two minor streams are switched back and forth into the main stream to provide either a pure helium or a He/O_2 atmosphere in the oven. A 1 ml loop and a Carle valve are used to inject CH_4 into the carrier stream upstream of the oven during each sample analysis for calibration. A backflow stream (10% of the initial carrier stream) exits the front of the outside end of the sample oven to purge ambient air, which enters when samples are loaded, from

the oven. The back flow stream rejoins the carrier stream just ahead of the FID so that all calibration gas carried by the back flow stream will be measured by the FID.

The pyrolytic conversion correction system consists of a He/Ne laser, fiber optic light pipes, an optical quality quartz rod which goes through the center of the MnO_2 oven, a narrow band pass filter which discriminates against oven glow, and a photo-detector. Light from a He/Ne laser is conducted to the quartz rod by a fiber optic light pipe and illuminates the sample surface during the analysis procedure. Reflected laser light from the sample is conducted back down the quartz rod to a photo cell detector. The photo-detector signal is proportional to filter blackness.

Analysis Procedure: Samples are placed in a quartz boat which is then slid into sample oven at a precise time after the computer-controlled analysis program is started. The analysis proceeds automatically under computer control.

Thermo-optical correction for OC pyrolysis is accomplished as follows. The sample is continuously illuminated by laser light during the analysis and the intensity of the reflected light from the sample is measured with a photo-detector. It is assumed that the strength of the reflected signal is proportional to filter blackness and that this in turn is proportional to filter EC concentration. At the start of the analysis filter blackness is determined and is assumed to be a measure of the initial EC concentration present on the filter. The laser signal starts at an initial value and decreases as organic material on the filter is pyrolytically converted (by charring) to elemental carbon. When O_2 is introduced the laser signal increases as the filter becomes more reflective as EC is oxidized from the filter. When the filter returns to its initial blackness OC analysis ends and EC analysis begins.

Organic Carbon Analysis: The sample is heated in an atmosphere of He at temperature steps of 300, 450, and 650°C to vaporize organic carbon. The step heating program is used to minimize pyrolytic conversion of organic carbon to elemental carbon. After the sample OC emission rate drops to a low value at 650°C the sample oven temperature is decreased to 400°C and 2% O_2 is introduced into the carrier stream. OC that volatilizes at temperatures greater than 650°C might be recorded as EC with this system. The sample oven temperature is then gradually increased and finally held at 750°C for elemental carbon analysis. The endpoint of organic carbon analysis is determined by the point at which the filter returns to its initial blackness following the introduction of O_2 into the carrier stream. It is assumed that pyrolized organic carbon has the same light absorbance as the elemental carbon initially loading the filter. This system also compensates for elemental carbon that might be removed from the filter by trace amounts of O_2 in the helium carrier stream used during OC analysis.

Elemental Carbon Analysis: EC analysis follows OC analysis. The measurement of initial EC starts after the filter has returned to its initial blackness after pyrolized organic carbon has been oxidized. EC measurement is concluded when the sample stops emitting carbon at 750°C. EC that does not oxidize at 750°C will not be detected by this system.

Total Carbon Analysis: TC = OC + EC

Carbonate Carbon Analysis: Can be done as a separate analysis.

Calibration Standards: Internal standard--nominal 5% CH_4 in helium (used at the end of every analysis). External standard--aqueous sucrose or potassium hydrogen phthalate solutions containing a known mass of standard per unit volume of solution (used occasionally).

Measurement range: 0.2 - 750 $\mu g/cm^2$
Minimum detection limit: 0.2 $\mu g/cm^2$
Nominal Accuracy: TC: 5%.
Nominal Precision: OC: 5-10% (8.4% for round robin results)   EC: 5-10% (6.9% for round robin results)   TC: 4% (7% for round robin results)

12. (Sunset Laboratory (SL)

Method: Thermal Optical Transmission

Sample: 1x1.5 cm

Species Measured: OC and EC

System Description: This system is an improved version of the OGI system.

Analysis Procedure: This system is similar to the OGI system in its flow configuration and computer control system. A rectangular sample is place horizontally in a boat which can be moved into the sample heating oven. During the heating process in the sample oven a He/Ne laser beam is directed through the filter sample. The transmitted beam intensity is monitored by a photocell. Variation in transmitted beam intensity is related to filter EC loading. As in the OGI system, carbon evolved from the sample after EC oxidation has started and when the blackness of the filter equals its initial blackness is classified as initial EC deposited on the filter.

As organic compounds are vaporized, they are immediately oxidized to CO_2 in an oxidizing oven directly downstream of the sample oven. The CO_2 in helium is then converted to methane in a nickel catalyst methanator and subsequently detected by a flame ionization detector.

Organic Carbon Analysis: In a completely oxygen-free helium atmosphere, the sample is heated in four temperature steps to 650°C to volatilize OC from the filter. The laser system measures the original filter blackness and continually monitors filter blackness. OC analysis ends when the filter returns to its initial blackness after the presence of O_2 in the carrier stream starts to oxidize EC.

Elemental Carbon Analysis: Carbon detected after the laser system notes that the sample has returned to its initial blackness is recorder as EC. EC analysis is concluded after the sample is held at 800°C for a sufficient time to oxidize all visible EC.

Total Carbon Analysis: $TC = OC + EC$

Carbonate Carbon Analysis: maximum carbonate estimate is given by OC output during the 500-650°C temperature phase during OC analysis.

Measurement Range: OC: 5-200 $\mu g/cm^2$; EC 1-15 $\mu g/cm^2$
Minimum detection limit: 0.2 $\mu g/cm^2$
Nominal Accuracy: TC: 4-6%.
Nominal Precision: OC: 4-6%   EC: 4-6%   TC: 4-6%

13. University of Minnesota (UM)

Method: Thermal (McMurray, P. H. and Zhang, X. Q., 1988)

Species Measured: TC only (For round robin OC and EC were done by EMSI).

System Description: The system consists of a sample heating furnace, in which the temperature can be increased from 100-600°C, followed by a catalytic furnace which oxidizes carbon compounds to CO_2. CO_2 is measured by a Horiba VIA-500 non-dispersive infrared CO_2 analyzer. The system is controlled by a Zenith 158 personal computer.

Analysis Procedure: Samples are placed in a quartz boat and inserted into furnace 1 which is initially at a relatively cool temperature (about 100°C). Oxygen is then allowed to flow over the sample as the temperature of this furnace is ramped at a constant rate to 600°C over a 20 minute period. At the completion of the ramp the furnace temperature is maintained at 600°C for 3 minutes to burn any residual carbon before being cooled back to the original temperature for another analysis. Temperature of the ramping furnace is controlled with an Omega programmable controller.

A second furnace is located downstream of furnace 1. This furnace is maintained at about 800°C and is packed with MnO_2. This furnace ensures complete combustion (to CO_2) of volatiles of CO which might leave furnace 1. The CO_2 leaving furnace 2 is measured with the Horiba NDIR CO_2 analyzer. An automated computer-driven data acquisition system is used to record and store all data for later analysis. The data acquisition system consists of a Data Translation DT2901 data acquisition board in a Zenith 158 personal computer.

The mass of carbon on samples is determined by numerically integrating the amount of CO_2 detected with the Horiba detector.

Organic Carbon Analysis: Not measured

Elemental Carbon Analysis: Not Measured

Total Carbon Analysis: Sample heated to 600°C in an atmosphere of 2% O_2/98% He.

Standards: di-octylphthalate (DOP) and graphite

Measurement range: 400 μg
Minimum detection limit: 1 μg
Nominal Accuracy: TC: 10%.
Nominal Precision: TC: 5%